T. K. Veselovskaya, I. V. Machinskaya,
N. M. Przhiyalgovskaya

PROBLEMS AND EXERCISES IN ORGANIC CHEMISTRY

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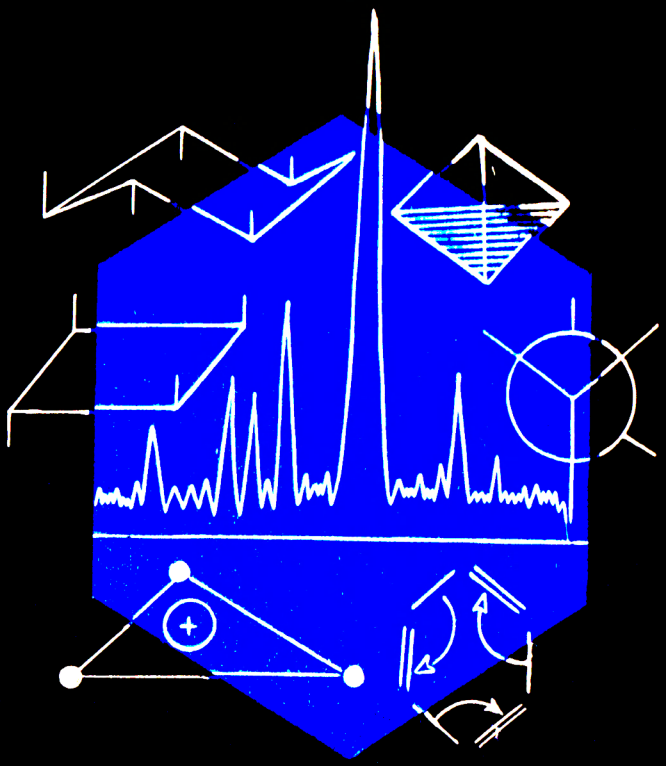

ИЗДАТЕЛЬСТВО
МИР

Т. К. ВЕСЕЛОВСКАЯ, И. В. МАЧИНСКАЯ,
Н. М. ПРЖИЯЛГОВСКАЯ

ВОПРОСЫ И ЗАДАЧИ ПО ОРГАНИЧЕСКОЙ ХИМИИ

под редакцией
проф. Н. Н. Суворова

ИЗДАТЕЛЬСТВО «ВЫСШАЯ ШКОЛА» МОСКВА

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PREFACE

New developments in the subject and in the scope of the course in organic chemistry now given to students, depend largely upon the remarkable advances which have occurred in the theory of organic chemistry. A series of comprehensive textbooks and manuals were published in which the structure and properties of organic compounds are presented in new theoretical contexts. Among these are such works as: *Fundamentals of Organic Chemistry** by A. N. Nesmeyanov and N. A. Nesmeyanov, vols. I-IV, *Basic Principles of Organic Chemistry* by J. Roberts and M. Caserio, *Chimie Organică* by C. D. Nenițescu.

As regards textbooks concerning problems and exercises in organic chemistry, most of them unfortunately do not devote sufficient attention to modern theory, except the book *Problems and Exercises in Organic Chemistry* by A. E. Agronomov**. But it is mainly intended for university students, while many other Soviet institutes that educate future chemical engineers, rather than researchers, still need a special textbook for their students.

The present book differs substantially from previously published ones in that its practical problems are closely connected with modern theory. Properties of compounds from each class are considered with respect to chemical bonds, and spatial and electronic structure of molecules. Special attention is given to conditions under which organic

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* Translated into English by Mir Publishers in 1976-1978.

** Translated into English by Mir Publishers in 1974 (reprinted in 1977).

reactions take place, their mechanisms, and the ways by which structural factors affect the reactivity of organic compounds. Special importance is attached to physical methods of investigating organic compounds. Hence the textbook contains problems dealing with I-R, U-V, and NMR spectra of compounds from different classes.

This textbook differs in that, in addition to usual problems and exercises, it also contains questions which, in the authors' opinion, will call the student's attention to the main aspects of theoretical organic chemistry and will hence facilitate his learning.

Considering the practical character of this book, the authors compiled their problems and exercises so that they can be given as control tasks to different students. Hence there are series of similar problems on certain subjects that are variations of a typical model and differ only in the object or in the approach to a problem.

More difficult problems and exercises, as well as those extending beyond the limits of the program, are marked with an asterisk and their solution is given at the end of the book.

Along with trivial and rational names, the textbook gives also modern nomenclature according to the IUPAC system. The absorption spectra of substances are given mainly according to Sadtler Standard Spectra. The Appendix contains also spectral tables.

The authors will be grateful for any constructive criticism concerning this textbook.

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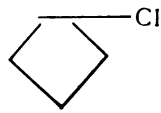
INTRODUCTION

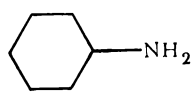
1. What is organic chemistry? For what reasons has organic chemistry been isolated into a separate subject?
2. Formulate the basic principles of the theory of chemical structure developed by A. M. Butlerov. Describe its importance for the development of organic chemistry.
3. What principles underlie the classification of organic compounds? By what characteristics can an organic compound be attributed to a series or a class?
4. To what series or class should the following compounds be attributed:

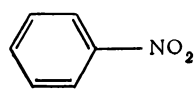
(a) divinyl, $CH_2=CH-CH=CH_2$

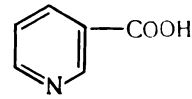
(b) isobutyl alcohol, $(CH_3)_2CH-CH_2OH$

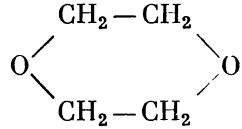
(c) acetone, $CH_3-CO-CH_3$ |

(d) chlorocyclopentane 

(e) cyclohexylamine 

(f) nitrobenzene 

(g) nicotinic acid 

(h) dioxane 

5. Characterize the role of quantum mechanical concepts in the development of our knowledge of the nature of a chemical bond.

6. Define the main types of chemical bonds: ionic and covalent. Indicate the physical causes that are responsible for the formation of bonds between atoms. Give examples of diatomic molecules:

(a) with an ionic bond, (b) with a covalent bond.

7. Characterize chemical bonds in molecules of the following compounds: (a) fluorine, (b) methane, (c) hydrogen bromide, (d) sodium fluoride, (e) sodium amide.

8. What is known as the donor-acceptor bond? Give examples of molecules with the donor-acceptor bonds.

9. Characterize chemical bonds in molecules of the following compounds: (a) carbon monoxide, (b) ammonium bromide, (c) nitric acid, (d) all oxides of nitrogen.

10. Give electronic structure of the following molecules and ions: (a) ammonia and NH_4^+ ion; (b) water, H_3O^+ ion, and OH^- ion; (c) bromine, Br^- anion, and Br^+ cation; (d) H_2, H^+, and H^-; (e) HNO_2, NO_2^-, NO_2^+, and NO^+.

11. Define the σ- and π-bonds. Give examples of organic and inorganic compounds whose molecules have: (a) only σ-bonds, (b) σ- and π-bonds.

12. Give electronic configurations of a carbon atom in the ground and excited state. How can the equivalence of all bonds in a molecule of methane be explained?

13. What kinds of hybridization are possible with the carbon atom? Characterize the form and spatial direction characteristics of the atomic orbitals.

14. Define chemical bonds in the following molecules: (a) ethane, (b) ethylene, (c) acetylene. Draw atomic-orbital diagrams of their structures.

15. What particles are known as free radicals? How do they differ from ions? Give examples of organic and inorganic free radicals.

16. Give electronic formulas for the following particles: (a) $CH_3\cdot$, (b) CH_3^+, (c) CH_3^-. In what state of hybridization is the carbon atom present in each of these particles?

17. Discuss the electronic and spatial structure of the following particles: (a) $CH_3-\dot{C}H-CH_3$, (b) $(CH_3)_3C^+$, (c) CN^-.

PART ONE

ALIPHATIC COMPOUNDS

CHAPTER ONE

SATURATED HYDROCARBONS (ALKANES)

A. Isomerism. Nomenclature

18. Formulate the concept of a homologous series. What is the general formula of the alkane series? Write molecular formulas of saturated hydrocarbons containing eight, twelve, and twenty carbon atoms.

19. Write structural formulas of the first ten hydrocarbons of the methane series having normal structure. Write formulas of primary hydrocarbon residues (alkyls) corresponding to each of these hydrocarbons. Name all these hydrocarbons and the corresponding alkyls.

20. What are isomers? Write structural formulas of all isomeric butanes, pentanes, and hexanes. Indicate the number of primary, secondary, and tertiary carbon atoms contained in each isomer of C_6H_{14}.

21. Write structural formulas of two close homologues of heptane having in their molecule (a) two tertiary carbon atoms and (b) one quaternary carbon atom.

22. How many alkyl isomers can be derived from hydrocarbons having the composition: (a) C_3H_8, (b) C_4H_{10}? Write their formulas and name them.

23. How many primary, secondary and tertiary alkyls correspond to the hydrocarbon having the structure

$$CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_2-CH_3?$$

Write their formulas.

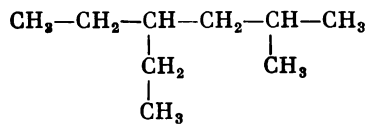
24. Formulate the principle according to which saturated hydrocarbons are given rational names. Name all isomers of hydrocarbons having the formulas: (a) C_4H_{10} and (b) C_5H_{12}.

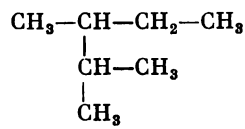
25. Write structural formulas of the following hydrocarbons: (a) tetramethylmethane, (b) methyldiethylmethane, (c) diisopropylmethane, (d) trimethylpropylmethane, (e) methyl-di-*tert*-butylmethane.

26. Write structural formulas of all isomers of heptane that can be derived from a hydrocarbon having the structure $CH_3—CH(CH_3)—CH_2—CH_2—CH_3$ by substituting the methyl group for the hydrogen atoms. Give their rational names.

27. Formulate the IUPAC principle of giving names to saturated hydrocarbons. Give IUPAC names to all hydrocarbons whose isomers have the composition: (a) C_5H_{12}, (b) C_6H_{14}.

28. What are IUPAC names of the following hydrocarbons:

(a)


(b)


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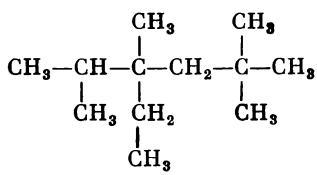

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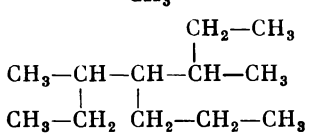
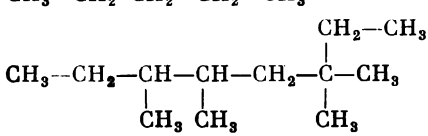
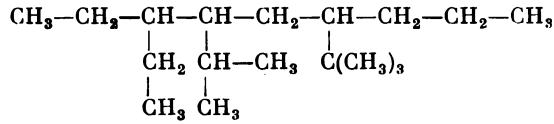
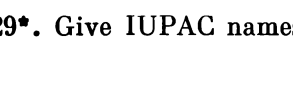
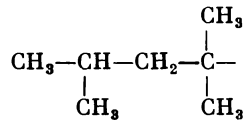
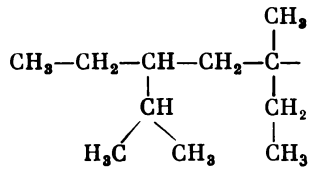


(e)


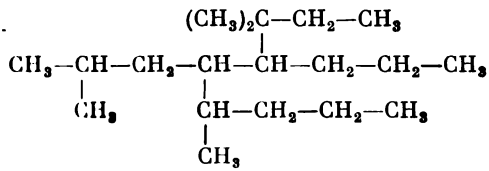
(f) 

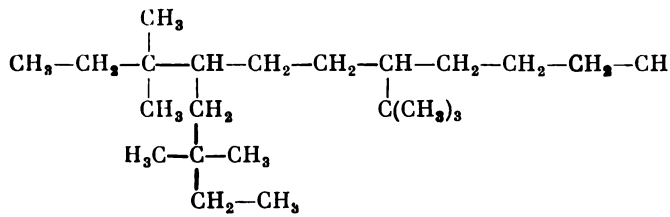
29*. Give IUPAC names to the following alkyls:

(a)  , (b) 

(c) 

30*. Give IUPAC names to the following hydrocarbons:

(a) 

(b) 

31. Consider the following names: (a) 2-ethylpentane, (b) 2,2,4-trimethylpentane, (c) 2,5,6,6-tetramethyl-5-ethyloctane. Are there mistakes in these names? Correct if any.

32. Write structural formulas of the following hydrocarbons: (a) 3-methyl-3-ethylpentane, (b) 2,4,6-trimethylheptane, (c) 2,2,4,4-tetramethyl-3,3-diethylpentane, (d) 2,5-dimethyl-4-propyl-4-isopropylheptane. What are their rational names?

33. Give IUPAC names to the following compounds: (a) dimethyldipropylmethane, (b) ethylisopropylbutylmethane, (c) triethyl-*tert*-butylmethane, (d) dimethyl-*sec*-butylisobutylmethane.

B. Methods of Preparing

34. List the main natural sources of saturated hydrocarbons.

35. What methods of manufacturing artificial liquid fuels do you know?

36. Obtain butane and 2,2,4-trimethylpentane by catalytic hydrogenation of corresponding unsaturated hydrocarbons. Name the hydrogenation catalysts used in the reaction.

37. What reagents should be used to convert the compounds

(a) $CH_3CH_2CH_2CH_2CH_2OH$ and (b) $CH_3CH_2CH(CH_3)CH_2I$

into saturated hydrocarbons having the same structure of the carbon skeleton? Write reaction equations.

38. Use the Wurtz reaction to obtain (a) *n*-octane, (b) *n*-decane, (c) 2,3-dimethylbutane, (d) 3,4-dimethylhexane. Discuss the mechanism of the reaction. Compare the direction of polarization of the carbon-halogen and carbon-metal bonds.

39. What hydrocarbons can be prepared by the action of sodium on a mixture of ethyl iodide and propyl iodide?

40. What halogen-substituted compounds can be used to obtain *n*-hexane by the Wurtz reaction? Describe the most rational method of its synthesis.

41. Obtain the corresponding saturated hydrocarbons from the following organomagnesium compounds:

(a) $CH_3—CH_2—CH_2—MgBr$, (b) $CH_3—\underset{\displaystyle CH_3}{\underset{|}{CH}}—CH_2—MgI$

42. Write the process for preparing ethane by electrolysis of an aqueous solution of a potassium salt of the corresponding carboxylic acid. Discuss the mechanism of the reactions that take place at the anode and the cathode.

43. What hydrocarbons can be obtained by electrolysis of an aqueous solution of sodium salts of (a) propionic acid,

(b) butyric acid, (c) isobutyric acid? Write the equations of the reactions.

44. Write equations for the following conversions:

(a) $CH_3CH_2COOH \longrightarrow CH_3-CH_3$

(b) $CH_3CH_2COOH \longrightarrow CH_3-CH_2-CH_2-CH_3$

(c) $CH_3-(CH_2)_{16}-COOH \nearrow CH_3-(CH_2)_{15}-CH_3$, $\searrow CH_3-(CH_2)_{32}-CH_3$

45. What hydrocarbons will be obtained from $(CH_3)_3C-CH_2-COOH$: (a) by electrolysis of its sodium salt, (b) by heating its salt with solid alkali?

46. Write reactions of preparing 2,5-dimethylhexane: (a) by the Wurtz method, (b) by hydrogenation of the corresponding olefins, (c) by decarboxylation of the corresponding carboxylic acid.

47. Suggest a method for preparing 2,3-dimethylbutane from compounds containing 3, 4, 6, and 7 carbon atoms in their molecules.

48. Write reactions for preparing paraffins in which the number of carbon atoms is (a) doubled, (b) remains the same, (c) becomes one unit less.

49. Write reactions used for preparing methane in the laboratory.

C. Structure and Properties

50. What is the valence state of carbon atoms in saturated hydrocarbons? What is characteristic of this state?

51. Draw atomic-orbital diagrams of the molecular structure of the following compounds: (a) methane, (b) ethane, (b) propane.

52. Characterize the bonds C—C and C—H in saturated hydrocarbons (length, energy, polarity, polarizability). What conclusion concerning the reactivity of alkanes can be drawn?

53. What feature of the electronic structure of ordinary C—C bonds of paraffins accounts for the rotation of molecule parts about this bond? Is this absolutely free rotation?

54. What is understood by 'conformation' of a molecule? How many extreme conformations are possible with a mole-

cule of ethane? How can they be described? What is the cause of greater stability of one of these conformations?

55. Draw a curve describing the changes in potential energy of ethane molecule depending on the angle of rotation of one methyl group with respect to the other. To what conformations do the energy minimum and maximum correspond? What is the magnitude of the energy barrier for the extreme conformations of ethane?

56*. How many extreme conformations are possible for a molecule of (a) propane, (b) 2,2,3,3-tetramethylbutane? Draw them. Which conformations are more stable?

57. How many extreme conformations are possible for a butane molecule? Draw them in the form of perspective sawhorse formulas, and also after Newman. Indicate the most stable of them.

58*. How many odd conformations correspond to 1,2-dichloroethane? Why does the dipole moment of this compound grow with temperature?

59. Explain why tetramethylmethane (b.p. 9.4°C) boils at lower temperature than isopentane (b.p. 27.8°C) and *n*-pentane (b.p. 36.1°C).

60. Characterize the infra-red spectra of saturated hydrocarbons. What absorption bands can be considered characteristic?

61. Indicate characteristic absorption bands due to valence and deformational oscillations of various C—H bonds in the infra-red spectrum of *n*-octane (liquid film) (see Fig. 1).

62. Explain why alkanes are often used as solvents to take ultra-violet spectra of other compounds.

63. Define the concepts of homolytic (radical) and heterolytic (ionic) reactions. What properties of bonds account for their homolytic or heterolytic cleavage? Specify the conditions promoting radical and ionic reactions.

64. Explain why radical substitution reactions are characteristic of saturated hydrocarbons.

65. Write the reaction of chlorination of methane in the light. Consider the mechanism of the reaction. What are practical uses of methane chlorination products?

66*. Using the value of bond energy (see Appendix, Table 1) explain why methane is chlorinated according to equa-

tion (a) and not (b):

(a) $CH_3—H+Cl\cdot \longrightarrow CH_3\cdot +HCl$

(b) $CH_3—H+Cl\cdot \longrightarrow CH_3Cl+H\cdot$

67*. Using methane as an example, explain the dependence of the course of alkane halogenation on the nature of the halogen. To calculate ΔH, use the energy of bond dissociation (see Appendix, Table 1).

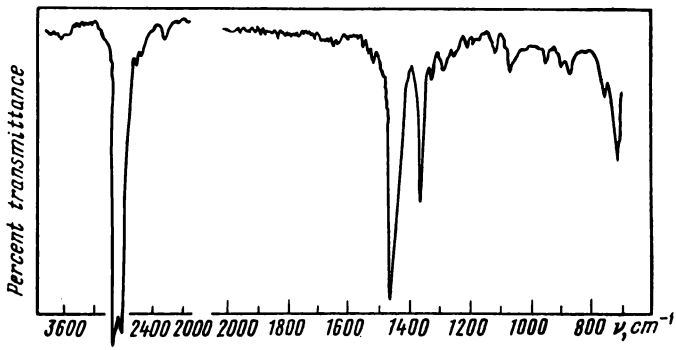


Fig. 1. I-R spectrum of *n*-octane

68*. Decide whether the following reaction can occur:

$$CH_3—CH_3+Br\cdot \longrightarrow CH_3—Br+CH_3\cdot$$

69. Use the methyl radical as an example to characterize the electronic and spatial structure, and also properties of simple free aliphatic radicals. How was their existence first proved?

70. Which of the radicals that follow below is the most stable?

(a) $CH_3—\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}\cdot$, (b) $CH_3CH_2CH_2CH_2\cdot$, (c) $CH_3—\dot{C}H—CH_2CH_3$

Develop your reasons.

71. What hydrocarbon radicals can be formed as intermediate particles during monochlorination of isopentane? Which is the most stable of them? In which direction is the reaction rate the fastest?

72*. Photochemical monochlorination of isopentane gives a mixture of 50 per cent of primary, 28 per cent of secondary and 22 per cent of tertiary chlorine derivatives. What is the relative reactivity of primary, secondary and tertiary C—H bonds in the chlorination reaction?

73*. Calculate the isomeric composition of mixtures formed by bromination in the gaseous phase at a temperature of 127°C of: (a) butane, and (b) isobutane. The relative reactivity of primary, secondary and tertiary C—H bonds is 1 : 32 : 1600, respectively. Explain why bromination of alkanes is a more selective reaction than chlorination.

74. Write the reaction of isobutane nitration by the Konovalov method. Consider the mechanism of the reaction.

75. Which of the two hydrocarbons, *n*-hexane or 2-methylpentane, is easier to nitrate by the Konovalov reaction? Develop your reasons.

76. Write the reaction of dodecane sulphochlorination. Discuss the mechanism of the reaction. What are the practical uses of the reaction products?

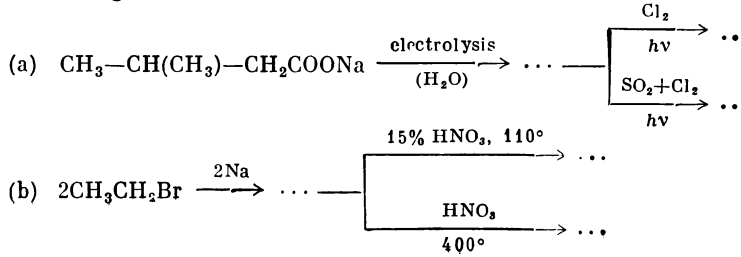
77. Sulphochlorination of alkanes gives chlorine derivatives of hydrocarbons as side products. Explain.

78. What are the conditions for oxidation of saturated hydrocarbons? What oxidation products have industrial importance?

79. What is the essence and practical importance of the cracking process? What chemical reactions are characteristic of this process? Consider the mechanism of these reactions using butane as an example.

80. What hydrocarbons are constituent parts of petrol? What properties of petrol account for its use as a fuel in internal combustion engines?

81. Indicate what compounds can be prepared by the following conversions:



D. Establishing the Structure of Organic Compounds by Their Properties

82. Write a structural formula of the hydrocarbon C_6H_{14} that gives only two monobromine derivatives on bromination.

83*. Establish the structure of the hydrocarbon C_9H_{20} by its NMR spectrum in which the intensities of two singlets (δ_1 0.98 ppm and δ_2 1.26 ppm) relate as 9 : 1.

84. Establish the structure of the hydrocarbon C_6H_{14} that is monobrominated into a tertiary derivative having the composition $C_6H_{13}Br$; the hydrocarbon C_6H_{14} can be prepared by the Wurtz and Kolbe reaction (without side products).

85. What is the structure of C_8H_{18} if: (1) it can be prepared by the Wurtz method from a primary alkyl halide as the only reaction product, and (2) a tertiary nitro compound is obtained by nitrating the hydrocarbon by the Konovalov method.

86. What is the structure of a carboxylic acid having the following properties: (1) electrolysis of an aqueous solution of its sodium salt gives the hydrocarbon $C_{10}H_{22}$; (2) decarboxylation of this acid gives tetramethylmethane?

CHAPTER TWO

ALKENES

A. Structural Isomerism. Nomenclature

87. Write structural formulas of all alkene isomers having the composition C_4H_8, C_5H_{10}. Name them according to the rational and IUPAC systems.[1]

88. Name the following compounds:

(a) $CH_2=CH-CH_2-CH_2-CH_2-CH_3$

(b) $CH_3-CH_2-CH=CH-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_3$

(c) $CH_3-\overset{\displaystyle CH_3}{\overset{|}{C}}=\overset{\displaystyle CH_3}{\overset{|}{C}}-CH_3$

(d) $CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH=CH-CH_2-\overset{\displaystyle CH_3}{\overset{|}{\underset{\displaystyle CH_3}{\underset{|}{C}}}}-CH_3$

89. Name the radicals: (a) $CH_2=CH-$, (b) $CH_2=CH-CH_2-$, (c) $CH_2=\overset{\displaystyle CH_3}{\overset{|}{C}}-$

90. Write structural formulas of isopropylethylene, sym-di-*tert*-butylethylene, and tetraethylethylene. Give their IUPAC names.

91. Check whether or not the hydrocarbons 5-hexene, 2-ethyl-2-butene, 2,3-diethyl-2-butene, and 2,6-dimethyl-4-octene are given correct names in accordance with the IUPAC nomenclature. Correct mistakes if any.

B. Methods of Preparing

92. Indicate industrial methods for manufacturing olefins. Give examples.

93. Characterize the processes occurring during cracking of saturated hydrocarbons. What compounds can be obtained by cracking butane or pentane?

94. Write the reactions of dehydrogenation of butane and isopentane. Specify the conditions for these reactions.

95. What methods of alcohol dehydration do you know? Name the catalysts used for homogeneous and heterogeneous dehydration.

96. Write the reaction of dehydration of butyl alcohol in the presence of sulphuric acid.

97. Name alkenes that can be obtained by dehydration of the following alcohols: (a) $CH_3CH_2CH_2CH_2OH$, (b) CH_3—$CH(OH)$—CH_2CH_3, (c) CH_3—CH_2—CH_2—$C(OH)$—CH_3, with CH_3 as a branch on the second carbon, (d) CH_3—$CH(CH_3)$—$C(OH)(CH_3)$—CH_3. Formulate the Zaitsev rule.

98. Obtain ethylene series hydrocarbons from 1-bromobutane, 1-chloropentane, 2-chloromethylpropane, and 2-iodo-2-methylbutane. Write the reactions. Name the obtained alkenes.

99. Write the reactions by which the corresponding olefins are obtained from 1,2-dibromopropane and 2,3-dibromobutane.

100. Obtain propylene from methylacetylene.

101. Write all known reactions by which 2-butene can be obtained.

C. Nature of Double Carbon-Carbon Bond. Geometric Isomerism (*cis-trans* Isomerism)

102. Characterize the second valence state of the carbon atom. Draw atomic-orbital model of propylene molecule. Compare the character of formation of σ- and π-carbon-carbon bonds.

103. Compare the length, energy, polarity, and polarizability of single and double carbon-carbon bonds. What bond has greater reactivity?

104. Characterize the distribution of electron density in molecules of ethylene and propylene. What accounts for the presence of the dipole moment in unsymmetrical olefins?

105. What accounts for the higher polarizability of the double carbon-carbon bond? How does it affect the molecular refractivity of olefins? What is understood by the double bond increment?

106*. What property of the double bond structure accounts for the appearance of geometric isomerism in the alkene series? *cis-trans* Isomerization of alkenes requires more energy compared with the interconversion of conformations in alkanes. Why?

107. Specify structure characteristics of alkenes having geometric isomers.

108. What is the difference between 'conformation' and 'configuration' of a molecule? Which of the compounds given below can exist in *cis-* and *trans*-configurations?

(a) $CH_3-CH_2-CH=CH-CH_2-CH_3$,

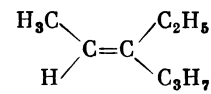
(b) $CH_3-\underset{\displaystyle CH_3}{\underset{|}{C}}=CH-CH_2-CH_3$

(c) $CH_3-CH_2-CH(CH_3)-CH=CH-CH(CH_3)-CH_2-CH_3$

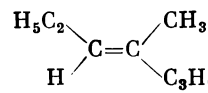
(d) $CH_3-CH_2-\underset{\displaystyle CH_3}{\underset{|}{C}}=\underset{\displaystyle CH(CH_3)_2}{\underset{|}{C}}-CH_2-CH_2-CH_3$

Write projection formulas of the *cis-* and *trans*-isomers.

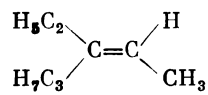
109. Indicate geometric isomers among compounds given below



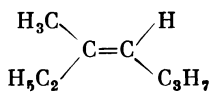
(a)



(b)



(c)



(d)

110. Do geometric isomers differ by melting and boiling points, density, or dipole moments? Explain.

111*. The dipole moments of *cis-* and *trans*-sym-dichloroethylene are (D): 1.89 and 0.0, respectively. Explain the difference.

112*. Heats of hydrogenation of stereoisomeric 2-pentenes are 119.74 and 115.56 kJ/mol. Which of these values refers to the *trans*-isomer?

113. Which of stereoisomeric symmetric di-*tert*-butylethylenes is more stable? Develop your reasons.

D. Properties

114. What absorption bands in the infra-red spectrum are characteristic of alkenes?

115. Distinguish between the bands produced by the valence and deformational oscillations of various bonds in the infra-red spectrum of 1-pentene (Fig. 2).

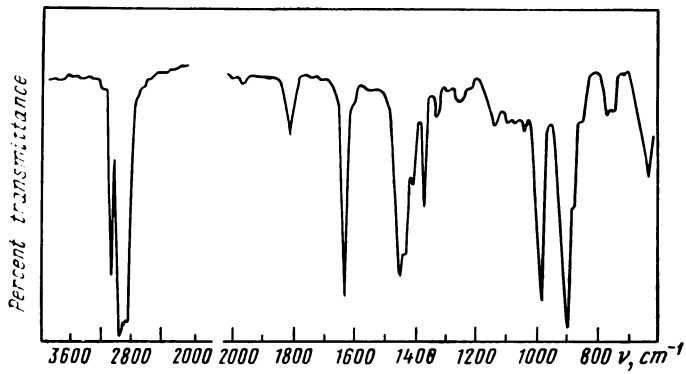


Fig. 2. I-R spectrum of 1-pentene

116. Is it possible to distinguish between 1-hexene and 3-hexene by their infra-red spectra?

117. Give the general characteristics of chemical properties of alkenes. Reactions of what type are most characteristic of them?

118. Write the reaction of hydrogenation of 2-butene, 4-methyl-2-pentene. Indicate the catalysts used in the reactions. What role do the catalysts play in the process of heterogeneous catalysis?

119. Write structural formulas of all ethylene hydrocarbons that form 3,4-dimethylhexane by the hydrogenation process. Give their IUPAC names.

120. Compare the character of bromine reaction with the following compounds:

$$CH_3-\underset{\displaystyle CH_3}{\overset{\displaystyle |}{C}}=CH-\underset{\displaystyle CH_3}{\overset{\displaystyle |}{CH}}-CH_3 \quad \text{and} \quad CH_3-\underset{\displaystyle CH_3}{\overset{\displaystyle |}{CH}}-CH_2-\underset{\displaystyle CH_3}{\overset{\displaystyle |}{CH}}-CH_3$$

Write balanced equations for the reactions.

121*. Write a balanced equation for the reaction in which bromine combines with propylene in the presence of water. Consider the mechanism of the reaction. Define the concepts of 'electrophilic reagent' and 'electrophilic addition reaction'. What facts prove the electrophilic character of bromine addition to olefins?

122*. Consider the mechanism of electrophilic addition of bromine to 2-butene. Which step of the reaction determines its rate? Prove: (1) the stepped character of the reaction; and (2) the formation of bromonium ion as an intermediate product.

123*. Bromine acts on ethylene in the presence of lithium chloride in methyl alcohol to give, in addition to 1,2-dibromoethane, also 1-chloro-2-bromoethane and 1-bromo-2-methoxyethane. Explain.

124. Arrange the halogens in the order of their decreasing activity in the reactions of addition at the double bond. Explain. Can alkane fluorides be obtained by adding fluorine to olefins?

125*. Which of the two compounds, ethylene or tetramethylethylene will add bromine easier? Develop your reasons.

126. 1,2-Dichloroethane is an important industrial product obtained by the radical addition of chlorine to ethylene. Specify the conditions of the reaction and consider its mechanism.

127. Write a balanced equation for the reaction of hydrobromination of 1-butene in the absence of oxygen or peroxides. Consider the mechanism of the reaction. Formulate the Markownikoff rule and explain it.

128. What compounds are formed by hydrobromination of the following substances in the absence of peroxides:

(a) $CH_2=CH-CH_2-CH_2-CH_2-CH_3$, (b) $CH_3-CH=C(CH_3)_2$

(c) $CH_3-CH=CH-CH_2-CH_3$, (d) $CH_2=CH-NO_2$

(e) $CH_2=CH-CF_3$

129*. In the series HI, HBr, and HCl, hydrogen iodide is the easiest to be added at the double carbon-carbon bond. Explain.

130. Write formulas of alkenes that are hydrochlorinated into the following compounds: (a) 2-chloro-2,4,4-trimethylhexane, (b) 3-chloro-3,4-dimethyl-4-ethylheptane.

131*. Explain why isobutylene readily adds hydrogen chloride, whereas ethylene does it only in the presence of catalysts, e.g. $AlCl_3$.

132*. Arrange the following alkenes in the order of their increasing reactivity in the hydrobromination reaction:

(a) $CH_3-CH_2-CH=CH_2$, (b) $CH_3CH_2-CH=CH-CH_3$

(c) $CH_3-\underset{\displaystyle CH_3}{\overset{\displaystyle |}{C}}=\underset{\displaystyle CH_3}{\overset{\displaystyle |}{C}}-CH_3$, (d) $CH_2=CH_2$

Give your explanations.

133*. Bearing in mind the mechanism of electrophilic addition reaction, write the product that will be formed by the action of iodine chloride (Cl—I) on propylene.

134. Write the compound that will be formed by the following conversions

$$CH_3CH_2CHBrCH_2Br \xrightarrow{Zn} \ldots \xrightarrow{HBr} \ldots \xrightarrow{Na} \ldots$$

135. Obtain trimethylethylene from isopropylethylene.

136. Continue the series of conversions given below:

$$CH_3-CHBr-CH(CH_3)-CH(CH_3)-CH_3 \longrightarrow$$
$$\longrightarrow CH_3-CH_2-C(CH_3)=C(CH_3)_2$$

137. Write a balanced equation for the reaction of hydrobromination of propylene in the presence of peroxides and consider the mechanism of the reaction.

138*. Why is the Kharasch effect observed, almost exclusively, in reactions with HBr and is practically absent with HI?

139. Explain why allyl bromide reacts in normal conditions with HBr to give 1,3-dibromopropane, but when it is thoroughly purified from oxygen and peroxides it forms 1,2-dibromopropane.

140. Accomplish the following transformations:

$$CH_3-CH=CH_2 \begin{cases} \nearrow CH_3-CH_2-CH_2-CH_2-CH_2-CH_3 \\ \searrow CH_3-CH(CH_3)-CH(CH_3)-CH_3 \end{cases}$$

141*. What compound is formed as ethylene is passed into water saturated with chlorine? Consider the mechanism of the reaction.

142. Complete the following:

$$Br{-}CH_2{-}CH_2{-}CH(CH_3){-}CH_3 \xrightarrow[(alcohol)]{KOH} \ldots \xrightarrow[(H_2SO_4)]{H_2O} \ldots$$

$$\ldots \xrightarrow[300°C]{Al_2O_3} \ldots \xrightarrow{HOCl} \ldots$$

Write the chemistry of the second and the last reactions.

143. What compounds are formed by the reaction of propylene, 1-butene, 2-hexene, 2-methyl-2-pentene with concentrated sulphuric acid (in the cold)? What are mechanisms of the reactions? Write a balanced equation for hydrolysis of the obtained products.

144. Suggest a method of chemical purification of 2,4-dimethylpentane from 2-hexene.

145. Write a balanced equation for hydration of isobutylene. Consider the mechanism of the reaction in conditions of acid catalysis. Why is isobutylene hydrated easier than the other isomeric olefins having the composition C_4H_8?

146. Hydration of what olefins will give (a) dimethylethylcarbinol, and (b) 2-butanol?

147. Compare the attitude of hexane and 1-hexene to heating in an aqueous solution of potassium permanganate.

148. Write balanced equations for the reactions of oxidation of trimethylethylene in which: (a) the double bond is cleaved, (b) glycol is formed, (c) the corresponding α-oxide is formed. What oxidant is used in each of these processes?

149. What products are formed by oxidation of each isomer of butylene with chromic acid?

150. Write a balanced equation for the reaction of oxidation of 2-hexene by the Prilezhaev method. Indicate the importance of this reaction.

151. Write the reaction of ozonolysis of 1-pentene, 3,4-dimethyl-3-hexene, and 2-methyl-2-butene.

152. What reactions can be used to distinguish between the following isomeric compounds: (a) 2-methyl-2-pentene

and 3-methyl-2-pentene, (b) tetramethylethylene, and α,β-methylisopropylethylene?

153. Write the structural formula of an ethylene hydrocarbon, the ozonolysis of which gives a mixture of methyl ethyl ketone and propionic aldehyde.

154. Ozonolysis of an alkene gives butyric aldehyde as a sole reaction product. What is the structural formula of the alkene?

155. Define the following terms: monomer, dimer, oligomer, polymer, degree of polymerization.

156. Formulate the concepts of stepped polymerization, and chain polymerization. Which of these processes gives high-molecular-weight compounds?

157. Write the dimerization of isobutylene in the presence of H_2SO_4. Consider the mechanism of the reaction.

158. Consider the mechanism of polymerization of ethylene in the presence of benzoyl peroxide.

159. What industrial methods of manufacturing polyethylene do you know?

160. Name the most important polymers manufactured on the basis of olefins.

161. Write the reaction of telomerization of ethylene with carbon tetrachloride. Consider its mechanism.

162. Why do olefins enter the reactions of allylic substitution? What is a mesomeric radical? Write the reaction of allylic chlorination of propylene at high temperatures. Consider the mechanism of the reaction.

163*. What compound will predominantly be obtained by monobromination of 2-methyl-2-pentene with N-bromosuccinimide? Write the reaction and explain it.

164. Write reactions of 2,2,4-trimethyl-3-hexene with chlorine: (1) at room temperature, (2) at 400°C. Compare the mechanisms of the reactions.

165. Write the reaction of oxidation of ethylene hydrocarbon having the structure $R—CH=CH—CH_2—R'$ with air in the presence of manganese salts.

166. Give an example of alkylation of saturated hydrocarbons with olefins.

E. Establishing the Structure of Organic Compounds by Their Properties

167. Write structural formula of the compound C_5H_{10} the ozonolysis of which gives a mixture of acetone and acetic aldehyde.

168. What is the structure of the hydrocarbon $C_{10}H_{20}$ the ozonolysis of which gives valeric aldehyde as the only reaction product?

169. Dehydration of two isomeric alcohols (I) and (II) having the molecular formula $C_8H_{18}O$ gives the same ethylene hydrocarbon. Energetic oxidation of the latter gives a mixture of acetone and valeric acid. What are the structural formulas of the starting alcohols (I) and (II)?

170*. Full hydrogenation of 2.8 g of unsaturated hydrocarbon, having the molecular weight 140, requires 448 ml of hydrogen at STP. To what homologous series does this hydrocarbon belong?

171*. Write the molecular formula of an alkene, whose 2.24 g add 3.20 g of bromine.

172. Hydrocarbon C_5H_{10} absorbs at 1658 cm^{-1} in the infra-red region of the spectrum. When hydrogenated, it gives *n*-pentane, and when oxidized it gives a mixture of acids having the formula R—COOH. What is the structure of the C_5H_{10} hydrocarbon?

173*. Write the structural formula of the hydrocarbon C_8H_{16}, having the following properties: (1) when acted upon by N-bromosuccinimide, it gives a tertiary halogen derivative, (2) when hydrogenated it gives a hydrocarbon that can be obtained as the only reaction product from a primary alkyl halide by the Wurtz reaction.

174*. Establish the structural formula of the hydrocarbon C_5H_{10} by the wavelengths of its infra-red spectrum: 3090, 2960, 1640, 1460, 1375, 1370, 1000, and 920 cm^{-1}.

CHAPTER THREE

ALKADIENES

A. Isomerism. Nomenclature

175. Write structural formulas of all diene hydrocarbons having the composition C_5H_8. Give their IUPAC names. To what type of dienes do they belong?

176. Write structural formulas of propadiene, 1,3-butadiene, 1,5-hexadiene, 2,3-dimethyl-1,3-butadiene, and 1,7-octadiene.

177. Write structural formulas of the following hydrocarbons: (a) isopropyl allene, (b) divinyl, (c) diallyl, (d) isoprene. Give their IUPAC names.

178. Give IUPAC names to the following compounds:

(a) $CH_3-CH_2-CH=C=CH-CH_3$, (b) $CH_2=\underset{\displaystyle CH_3}{\underset{|}{C}}-CH_2-\underset{\displaystyle CH_2}{\underset{\|}{C}}-CH_3$

(c) $CH_2=CH-CH=CH-CH=CH_2$, (d) $CH_2=\underset{\displaystyle CH_3}{\underset{|}{C}}-\underset{\displaystyle CH_3}{\underset{|}{C}}=CH_2$

(e) $CH_2=CH-CH(CH_3)-CH(CH_3)-CH=CH_2$

179. Write structural formulas of all diene hydrocarbons that are hydrogenated into 2-methylpentane. Give their IUPAC names.

180*. How many geometric isomers should each of the following compounds have: (a) 1,4-pentadiene, (b) 1,3-pentadiene, (c) 2,4-hexadiene? Write the formulas of the geometric isomers.

181*. Draw formulas of the following geometric isomers: (a) *trans,trans*-3,5-octadiene, (b) *cis,cis*-3,5-octadiene, (c) *trans,cis*-3,5-octadiene.

B. Methods of Preparing

182. What industrial methods of manufacturing divinyl, isoprene, and chloroprene do you know?

183. Write the reactions of dehydration of (a) 1,4-butanediol, (b) 2,3-dimethyl-2,3-butanediol. Specify the reaction conditions. Name the reaction products.

184. Obtain diene hydrocarbons from the following compounds: (a) 1,3-butanediol, (b) 2,3-dibromo-1-propene, (c) 3,4-dibromo-1-hexene, (d) 1,3-dichloro-2-methylbutane.

185. Prepare 1,5-hexadiene by the Wurtz reaction and by the Grignard-Wurtz reaction.

186*. Suggest methods for preparing isoprene from isopentane.

C. Structure and Properties

187. Draw atomic-orbital models of the following compounds: (a) 1,2-pentadiene, (b) 1,3-pentadiene, (c) 1,4-pentadiene. Compare the character of π-bonds in these compounds. In which of these cases do the π-bonds interact? How does it show?

188. Show the S-*cis* and S-*trans* conformations of 1,3-butadiene. In which of the conformations does this compound exist under normal conditions?

189. Draw the atomic-orbital model of a 1,3-butadiene molecule. What effect does the structure of compounds with conjugated double bonds produce on the length of the single and double carbon-carbon bond? What effect does it produce on the chemical properties of the compounds?

190. What is known as the energy of conjugation? Give the value of the conjugation energy for 1,3-butadiene. How can it be determined?

191. Use the data of physico-chemical investigations to illustrate the mutual effect of double bonds in the molecule of 1,3-butadiene.

192. Characterize the absorption of ethylene and 1,3-butadiene in the ultra-violet region of the spectrum. How can the differences be explained?

193. What effect does the presence of conjugated bonds in the molecule of a diene produce on the magnitude of the molecular refractivity? Indicate which of the following dienes, 1,5-hexadiene or 2,4-hexadiene, has the greater molecular refractivity. What is the exaltation of molecular refractivity of a conjugated system of double bonds?

194*. Calculate the molecular refractivity (MR_D) of: (a) 1,5-hexadiene and (b) 2,4-hexadiene using the refractivities of covalent bonds (R_D): C—H 1.676, C—C 1.296, and C=C 4.17. Compare them with the following experi-

mentally found values MR_D: 28.99 for compound (a) and 30.64 for compound (b). Explain the differences between the experimental data for compounds (a) and (b).

195. What spectral method can be used to distinguish between 1,5-hexadiene and 1,3-hexadiene? Develop your reasons.

196. Consider the ultra-violet absorption spectra of the following hydrocarbons: (a) 2-methyl-1,4-pentadiene, (b) 2-methyl-1,3-pentadiene. Which of these compounds will be characterized by greater wavelength? Develop your reasons.

197. How can the structure of compounds with conjugated double bonds be represented? Describe the structure of 1,3-butadiene and 2,4-hexadiene using extreme structures. What distribution of electron density corresponds to the real molecule? Formulate the concept of mesomerism.

198*. Explain why the measured heat of hydrogenation of 1,4-pentadiene (254.56 kJ/mole) is two times that of 1-butene (126.86 kJ/mole), while with 1,3-butadiene it is only 239.07 kJ/mole.

199. Write equations for hydration of 1,3-butadiene: (a) by hydrogen in the presence of a catalyst, (b) by the action of sodium in alcohol. Consider the mechanism of the reactions.

200*. Compare the attitude of ethylene and 1,3-butadiene to sodium in alcohol. Explain the differences.

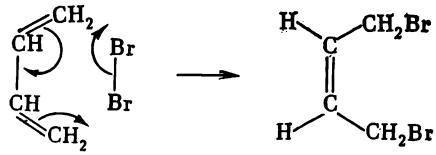
201*. What reaction products can be expected from treatment of 3,7-dimethyl-1,3,6-octatriene with sodium in alcohol with subsequent oxidation of the obtained product in rigid conditions?

202. What compounds are formed by the action of bromine on 1,4-pentadiene? Describe the mechanism of the reaction.

203*. Draw structural formulas of the products of selective addition of one mole of bromine to the following compounds: (a) $CH_3—CH=CH—CH_2—CH=CHBr$, (b) $(CH_3)_2C=CH—CH_2—CH=CH_2$.

204. Using 1,3-butadiene and chlorine, taken in the ratio of 1 : 1, characterize reactions of electrophilic addition to dienes with conjugated double bonds. Describe the mechanism of the reactions. What carbonium ion is known as mesomeric? Draw its structure.

205*. What experimental data disagree with the mechanism of simultaneous addition of bromine to both ends of the conjugated system:



206*. On what factors do the relative quantities of products of 1,2- and 1,4-addition in dienes with conjugated double bonds depend? What is understood by kinetic and thermodynamic control of the reaction?

207*. Characterize the reaction of 2,4-hexadiene with bromine (1 mole) under the following conditions: (a) at low temperature (—15°C) (kinetic control); (b) at room temperature (thermodynamic control).

208. What compounds are formed by energetic oxidation of the product of addition of one mole of bromine to 1,3-butadiene in the 1,2-positions? in the 1,4-positions?

209. What products are formed by the reaction of one mole of hydrogen bromide (in the absence of peroxides or oxygen, and at room temperature) with the following compounds: (a) 1,4-pentadiene, (b) 1,3-butadiene? Develop your reasons.

210. Write the reaction of 1,3-butadiene with HBr (1 mole) in the presence of a peroxide. Consider the mechanism of the reaction. Characterize the structure and properties of the formed mesomeric radical.

211. Accomplish the following transformations:

(a) $CH_2=CH-CH=CH_2 \longrightarrow ClCH_2-CHBr-CHBr-CH_3$

(b) $CH_2=CH-CH=CH_2 \longrightarrow BrCH_2-CH_2-CHCl-CH_2Br$

212. Write equations for diene synthesis using 2,3-dimethyl-1,3-butadiene as a diene, and (a) maleic anhydride, (b) acrolein as a dienophile.

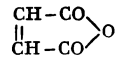
213*. What geometric isomer of 2,4-hexadiene wil be the easiest to enter the Diels-Alder reaction?

214*. Add 1,3-butadiene to tetracyanoethylene in tetrahydrofuran solution: a colourless crystalline product precipitates. What conjecture concerning the structure of this compound can be made? Write the equation of the reaction.

215. Complete the following:

$$CH_3-CH(CH_3)-CH_2-CH_3 \xrightarrow[\text{(light)}]{Br_2\ (1\ \text{mole})} \ldots \xrightarrow{NaOH\ (alcohol)} \ldots$$

$$\ldots \xrightarrow{Cl_2} \ldots \xrightarrow[\text{heat}]{2NaOH\ (alcohol)} \ldots \xrightarrow{} \ldots$$



216. Write all possible isomers of diene hydrocarbons having the composition C_5H_8. Will they have similar molecular refractivity? Which of them will take part in the Diels-Alder reaction?

217. Write the ozonolysis of: (a) 1,4-pentadiene, (b) 2,3-dimethyl-1,3-butadiene.

218. Write polymerization of isoprene with the formation of rubber. How was the structure of natural rubber proved?

219. Write the equation for polymerization of butadiene in the presence of sodium. Consider the mechanism of the reaction.

220. Describe the industrial method of manufacturing chloroprene rubber.

221*. Draw the structure of a unit of the polymer, the ozonolysis of which gives diketone $CH_3COCH_2CH_2COCH_3$. What is the structure of the starting monomer?

222. Write the equation for copolymerization of butadiene: (a) with acrylonitrile, and (b) with styrene. Indicate the practical importance of these copolymers.

223. Draw the configurations of chains of the polymer obtained from 1,3-butadiene by (a) *cis*-1,4-addition, and (b) *trans*-1,4-addition.

224. What is the configuration of a macromolecule of natural rubber? On what does the high elasticity of rubber depend?

225. Gutta-percha being *trans*-1,4-polyisoprene, draw the configuration of its chains. What accounts for the different properties of gutta-percha and natural rubber?

D. Establishing the Structure of Organic Compounds by Their Properties

226. Write the structural formula of the hydrocarbon C_5H_8 the ozonolysis of which gives malondialdehyde OHC—CH_2—CHO and formaldehyde.

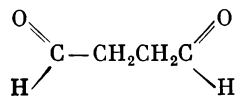
227. What is the structural formula of the hydrocarbon C_6H_{10} the ozonolysis of which gives a mixture of diacetyl $CH_3CO—COCH_3$ and formaldehyde?

228. Write the structural formula of a hydrocarbon that is formed by the action of sodium and alcohol on 3,5-dimethyl-1,3,7-octatriene. Give its IUPAC name.

229. The hydrocarbon $C_{11}H_{20}$ is oxidized into the following products: $CH_3CH_2COCH_3$, $HOOC—CH_2CH_2—COOH$, and CH_3CH_2COOH. What is its structure?

230. Establish the structure of C_6H_{10} if its reduction with sodium in alcohol gives a hydrocarbon, the ozonolysis of which gives a mixture of acetic and isobutyric aldehydes.

231. What is the structure of a monomer, whose product of polymerization is ozonolyzed into succinic dialdehyde:



232*. What is the structure of a compound having the formula C_4H_6, if its ultra-violet spectrum (in hexane) has the absorption band with λ_{max} at 217 mμ ($\varepsilon = 20{,}900$)?

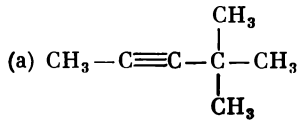
CHAPTER FOUR

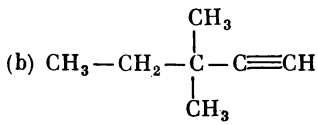
ACETYLENE HYDROCARBONS (ALKYNES)

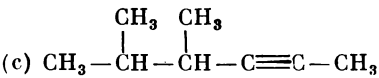
A. Isomerism. Nomenclature

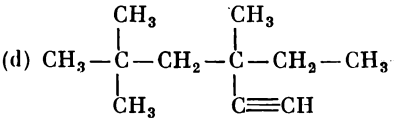
233. Derive structural formulas for all isomeric acetylene hydrocarbons having the molecular formula C_5H_8. Give their rational and IUPAC names.

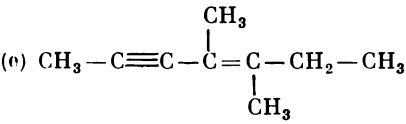
234. Give systematic names to the following compounds:

(a) 

(b) 

(c) 

(d) 

(e) 

235. Write structural formulas of the following acetylene hydrocarbons: (a) diisopropylacetylene, (b) *tert*-butylacetylene, (c) vinylacetylene, (d) *sec*-butylamylacetylene.

Give their IUPAC names.

236. Write structural formulas for all acetylene and diene hydrocarbons that are hydrogenated into 2-methylpentane. Name them.

237*. Give systematic names to the following compounds:

(a) $CH_3-C\equiv C-C\equiv C-C\equiv C-C\equiv C-CH=CH_2$

(b) $CH_3-CH=CH-(C\equiv C)_4-CH=CH_2$

B. Methods of Preparing

238. Name industrial methods of manufacturing acetylene.

239. What compounds are formed by the action of alkali solution in alcohol on 1,2-dibromobutane? on 1,1-dibromobutane? Write the reactions.

240. What dihalogen derivatives are required to prepare (a) propylacetylene, (b) methylisopropylacetylene, (c) divinylacetylene? Write these reactions.

241. Write the reactions by which the following acetylene hydrocarbons are obtained: (a) 2-butyne from 2-butene, (b) 1-pentyne from 1-pentanol.

242. Indicate the reagents by which the following conversions can be accomplished:

(a) $(CH_3)_2CH-CH=CH_2 \longrightarrow (CH_3)_2CH-C\equiv CH$

(b) $CH_3CH_2CH_2CH_2Br \longrightarrow CH_3CH_2C\equiv CH$

(c) $(CH_3)_2CH-CH_2-CH=CH_2 \longrightarrow (CH_3)_2CH-C\equiv C-CH_3$

(d) $CH_3-CH_2-CH_2-CH_2OH \longrightarrow CH_3-C\equiv C-CH_3$

243. What compound is formed by the successive action of sodium amide and ethyl iodide on 1-butyne?

244. Complete the following:

$$CH_3-CH_2-CH=CH_2 \xrightarrow{Br_2} \ldots \xrightarrow[heat]{KOH(alcohol)} \ldots$$

$$\ldots \xrightarrow[NH_3(liquid)]{NaNH_2} \ldots \xrightarrow{CH_3O\diagdown\diagup SO_2\ (CH_3O)} \ldots$$

245. Using the Grignard reaction obtain (a) diethylacetylene, (b) dipropylacetylene from acetylene.

246*. Write equations for conversions that occur at the cathode and anode during electrolysis of dipotassium salt of fumaric (or maleic) acid (KOOC—CH=CH—COOK).

C. Structure and Properties

247. What is the nature of the triple bond in acetylene from the viewpoint of modern science?

248. Characterize the third valence state of the carbon atom. Draw the structure of a molecule of methylacetylene using atomic orbitals.

249. Characterize the length, energy, polarity, and polarizability of the triple carbon-carbon bond. What conclusion concerning reactivity of compounds with triple bonds can be drawn?

250. Compare the carbon-carbon bond lengths in ethylene and acetylene. Explain the differences. How does it show on chemical properties of acetylene?

251. What absorption bands in the infra-red spectrum can be used to identify monoalkyl-substituted acetylenes?

252. Using the modern concept of the nature of ordinary and double carbon-carbon bonds, explain the presence of geometric isomers in alkenes of the R—CH=CH—R′ type and their absence in alkanes. Why do alkynes have no geometric isomers?

253*. How can the changes in acid properties in the series below be explained? Acetylene ($pK_a = 22$) > ethylene ($pK_a \approx 40$) > ethane ($pK_a > 40$).

254*. Explain why the acid properties of HCN are stronger than of acetylene.

255. Give balanced equations of the reactions that illustrate the activity of the hydrogen atom in acetylene and its monoalkyl homologues.

256. Name the following compounds and suggest methods for preparing them: (a) CaC_2, (b) $CH_3C{\equiv}CNa$, (c) $CH_3CH_2C{\equiv}CAg$, (d) $Cu{-}C{\equiv}C{-}Cu$, (e) $CH_3C{\equiv}C{-}MgBr$. How does water act on them? Write balanced equations of these reactions.

257. Which of the acetylene hydrocarbons given below will react with ammoniacal solution of cuprous oxide? (a) 1-butyne, (b) 2,5-dimethyl-3-hexyne, (c) 4-methyl-2-hexyne, (d) 3-methyl-1-hexyne. Write balanced equations for the reactions.

258. What reaction can be used to distinguish between propylacetylene and methylethylacetylene? How can these compounds be separated from each other?

259. What qualitative reactions can be used to distinguish between the following compounds: (a) $CH_3{-}C{\equiv}C{-}CH_3$ and $CH_3CH_2CH_2CH_3$; (b) $CH_3CH_2{-}C{\equiv}CH$ and $CH_2{=}CH{-}CH{=}CH_2$?

260*. Use spectral methods to distinguish between the following compounds given in pairs: (a) $CH_3CH_2C{\equiv}CH$ and

$CH_3—C\equiv C—CH_3$; (b) $CH_3CH_2—C\equiv C—CH_3$ and $CH_2=CH—CH=CH—CH_3$; (c) $CH_3CH_2—C\equiv CH$ and $CH_3CH_2—CH=CH_2$.

261*. The infra-red spectrum has absorption bands at 3300, 2950, 2860, 2120, 1465, and 1382 cm^{-1}. To what compound does this spectrum belong?

(a) $CH_3—CH_2—C\equiv C—CH_2—CH_2—CH_2—CH_3$

(b) $CH_3—CH_2—CH=CH—CH=CH—CH_2—CH_3$

(c) $CH_3CH_2CH_2CH_2CH_2CH_2—C\equiv CH$

262. Write balanced equations for reactions of partial and full hydrogenation of dimethylacetylene in the presence of a catalyst. Consider the mechanism and stereochemical orientation of the first step of the hydrogenation.

263*. Indicate which of the stereoisomers (*cis-* or *trans-*) will be obtained in the following reactions:

(a) $R—C\equiv C—R+H_2 \xrightarrow{\text{catalysis}} R—CH=CH—R$

(b) $R—C\equiv C—R+Br_2 \longrightarrow RCBr=CBr—R$

264*. Write structural formulas of products of partial and full hydrogenation of the following acetylene hydrocarbons: (a) 1-butyne, (b) 5-methyl-2-hexyne, (c) 2,6-dimethyl-4-octyne. Indicate the catalysts used for partial hydrogenation of alkynes. What is the configuration of the products obtained at the first step of hydrogenation of 1-butyne and 5-methyl-2-hexyne?

265. What acetylene hydrocarbons should be used for preparing the following halogen derivatives?

(a) $CH_3—CH_2—CBr_2—CHBr_2$, (b) $CH_3—CCl_2—CCl_2—CH_3$

Write balanced equations of the reactions. Consider their mechanisms.

266*. Explain why one mole of bromine acts on allyl acetylene to give dibromide $BrCH_2—CHBr—CH_2C\equiv CH$.

267. Accomplish the following conversions:

(a) $CH_3CH_2—C\equiv CH \longrightarrow CH_3CH_2—CClBr—CHClBr$

(b) $CH_3—CH=CH—CH_3 \longrightarrow$ *trans*-$CH_3—CBr=CBr—CH_3$

(c) $CH_3—CH_2—CH_2—CH_3 \longrightarrow CH_3—CBr_2—CBr_2—CH_3$

268. Write a structural formula of an acetylene hydrocarbon that reacts with hydrogen bromide to give: (a) 2-bromo-1-hexene, (b) 2,2-dibromo-3-methylbutane. Consider the mechanism of acetylene hydrocarbon reaction with HBr.

269*. How can the following transformations be accomplished?

(a) $CH_2Br—CH_2Br \longrightarrow CHBr_2—CH_3$

(b) $CH_3CH_2CHCl_2 \longrightarrow CH_3—CCl_2—CH_3$

(c) $CH_3CH_2CH_2CH_2OH \longrightarrow CH_3CClBr—CH_2CH_3$

270. What halogen derivatives can be obtained by the action of one mole of hydrogen bromide on *n*-butylacetylene: (a) in normal conditions, (b) in the presence of a peroxide? Consider the mechanisms of these reactions. What factors are important for the direction of the reaction in each case?

271*. Write the reaction between ethylacetylene and the acids: (a) HI, (b) HBr, (c) HOBr (two moles). Consider the mechanisms of the reactions.

272. Write structural formulas of carboxylic acids that are obtained by oxidation of 1-hexyne and 3-hexyne with chromic-sulphuric acid.

273. Arrange the hydrocarbons given below in the order of their increasing activity in electrophilic addition reactions: (a) propylene, (b) methylacetylene, (c) 2-methyl-2,4-pentadiene. Develop your reasons.

274. Write reactions of hydration of (a) acetylene, (b) isopropylacetylene, (c) diethylacetylene. Specify the conditions of the Kucherov reaction. What is its practical importance?

275. What compounds are formed by the action of water on 4-methyl-1-pentyne and on vinylacetylene in the Kucherov reaction?

276*. Write the reaction in which methyl ethyl ketone, $CH_3COC_2H_5$, is formed from 1-bromobutane.

277*. Write the reactions in which methylacetylene reacts with the following substances (in the ratio of 1 : 1): (a) hydrogen, in the presence of a catalyst, (b) bromine, (c) hydrogen bromide, (d) water, in the Kucherov reaction. What is the configuration of the compound obtained by the action of bromine on methylacetylene?

278. What compound is formed by the following transformations?

$$CH_3CH_2-CH=CH_2 \xrightarrow{+Br_2} \ldots \xrightarrow{2KOH,\ alcohol} \ldots \xrightarrow[(NH_3\ liquid)]{NaNH_2} \ldots \xrightarrow{CH_3I} \ldots \xrightarrow[(Hg^{2+};\ H^+)]{H_2O} \ldots$$

279. What reaction is known as vinylation? What products are obtained by the reaction of acetylene (in the presence of the corresponding catalysts) with the following substances: (a) HCN, (b) CH_3COOH, (c) C_2H_5OH?

280. Write the reactions between acetylene and formaldehyde, acetaldehyde, acetone? Specify the reaction conditions. Why are these reactions known as ethynylation?

281. Give examples of reactions of isomerization of alkynes that are accompanied (a) with transfer of the triple bond into the end of the hydrocarbon chain, (b) with transfer of the terminal triple bond. Specify the reaction conditions.

282. Describe industrial methods for the manufacture from acetylene of (a) acetic acid, (b) vinyl acetate, (c) vinyl chloride, (d) vinylacetylene, (e) propargyl alcohol, (f) 1,4-butanediol.

283. How can chloroprene rubber be manufactured from methane and inorganic reagents?

284. Write the reaction of preparing benzene from calcium carbide.

D. Establishing the Structure of Organic Compounds by Their Properties

285. What hydrocarbon having the composition C_6H_{10} is converted by energetic oxidation ($K_2Cr_2O_7+H_2SO_4$) only into propionic acid?

286. Write a structural formula of a hydrocarbon having the composition C_5H_8 that gives methyl isopropyl ketone in the Kucherov reaction.

287. Establish the structure of a hydrocarbon having the composition C_6H_{10} that can add four bromine atoms and that does not react with ammoniacal solution of cuprous oxide. When acted upon with water in the presence of a salt of mercury and sulphuric acid, said hydrocarbon gives

a mixture of methyl isobutyl ketone and ethyl isopropyl ketone.

288. Establish the structure of a compound having the composition C_4H_6, the infra-red spectrum of which has intense absorption bands at 3305 and 2110 cm^{-1}.

289*. What conversions can prove the structure of the compound C_6H_6, whose structural formula is $CH_2=CH-C\equiv C-CH=CH_2$?

290*. Determine the structure of a compound having the composition C_5H_8 reacting with ammoniacal solution of Cu_2Cl_2 to give a red precipitate; when heated with alcoholic alkali, it isomerizes into a hydrocarbon that, alongside with other reaction products, gives also acetone on oxidation.

CHAPTER FIVE

HALOGEN DERIVATIVES

ALKYL HALIDES
(CHLORIDES, BROMIDES, AND IODIDES)

A. Isomerism. Nomenclature

291. Write structural formulas of the following compounds: isopropyl bromide, *sec*-butyl chloride, *tert*-butyl iodide, amyl iodide, hexyl chloride, 1,3-dichloropropane, 1,2-dibromo-3-methylheptane.

292. Give IUPAC names to the following compounds:

(a) $CH_3CH(CH_3)CH_2CHBrCH_3$, (b) $CH_3CH_2CH(CH_3)CH_2CH_2I$

(c) $CH_3CH_2—\underset{\displaystyle CH_2I}{\underset{|}{CI}}—CH_3$, (d) $CH_3CHCl—\underset{\displaystyle CH_3}{\underset{|}{CH}}—CH_3$

293. Write structural formulas of all isomeric compounds of C_4H_9Br. Give their rational and IUPAC names.

294. Write structural formulas of all isomeric compounds having the composition $C_5H_{11}Cl$ and name them.

295. How many dichloro-substituted compounds can be obtained from *n*-pentane? Write their formulas and name them.

B. Methods of Preparing

296. Write the reaction of propane with chlorine. Consider the mechanism of the reaction. Can bromine-, iodine-, and fluorine-derivatives be produced by a similar way?

297. Write the reaction of preparing an alkane chloride using sulphuryl chloride as a halogenating agent.

298. Write balanced equations for the reactions of preparing *sec*-butyl chloride, *tert*-butyl bromide, 2,3-dibromopentane and 2,2-dichlorobutane from the corresponding unsaturated hydrocarbons.

299. Consider the conversion of propyl alcohol into propyl chloride and give equations for substitution of halogen for the hydroxyl group.

300. Accomplish the following conversions:

(a) $CH_3CH_2CHO \longrightarrow CH_3CH_2CHCl_2$

(b) $CH_3COCH_2CH_2CH_3 \longrightarrow CH_3CCl_2CH_2CH_2CH_3$

301. Write the reactions for preparing chloroform: (a) from acetone, (b) from ethyl alcohol, and (c) from acetylene.

302*. Which of the compounds given below will give the haloform reaction?

(a) $CH_3CH_2CH(OH)CH_3$, (b) $CH_3COCH_2CH_2CH_3$

(c) $CH_3CH_2CH(OH)CH_2CH_3$, (d) $(CH_3)_3C(OH)$

Write equations for the reactions.

303. Accomplish the following conversion:

$$CH_3CHClCH_2CH_3 \longrightarrow CH_3Cl_2CH_2CH_3$$

304. Complete the following:

$$CH_3{-}CHBr{-}CH_2{-}CH_3 \xrightarrow[\text{(alcohol, heat)}]{KOH} \cdots \xrightarrow{Br_2}$$

$$\longrightarrow \cdots \xrightarrow[\text{(alcohol)}]{2KOH} \cdots \xrightarrow[(Hg^{2+},\ H^+)]{H_2O} \cdots \begin{cases} \xrightarrow{PCl_5} \cdots \\ \xrightarrow{NaOH+I_2} \cdots \end{cases}$$

C. Properties

305. Characterize polarity and polarizability of the bonds C—H, C—Cl, C—Br, and C—I. Why are alkyl iodides characterized by the highest reactivity?

306. Characterize absorption of alkyl halides in the infra-red and ultra-violet regions of the spectrum. Give the values of chemical shifts of protons in the groups RCH_2Cl, RCH_2Br, RCH_2I and $RCHCl_2$.

307. Analyze the NMR spectrum of ethyl bromide (60 MHz, CCl_4; Fig. 3). Indicate which proton corresponds to each chemical shift. Explain the number of lines in resonance signals. What information carries the integral curve?

308. Give the pattern of NMR spectrum and the integral curve of 1,3-dichloropropane.

309*. What spectral methods can differentiate between

(a) $(CH_3)_3CCl$ and $(CH_3)_2CHCH_2Cl$
(b) $CH_3CH{=}CHCl$ and $CH_2{=}CH-CH_2Cl$?

310. What reductants can convert ethyl iodide into ethane? Write balanced equations of the reactions.

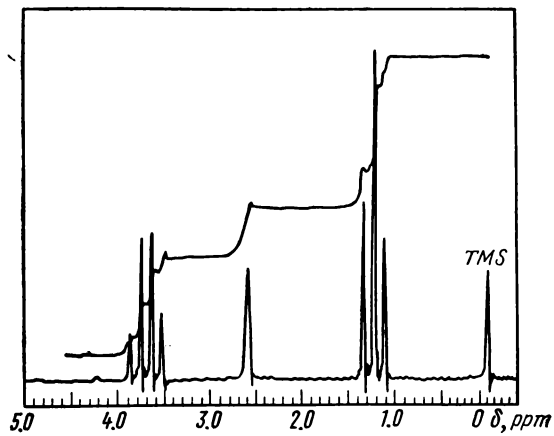
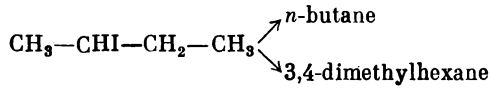


Fig. 3. NMR spectrum of ethyl bromide

311. Accomplish the following conversions:



312. Characterize the importance of alkyl halides as alkylating agents. Give examples of N- and O-alkylation with alkyl halides.

313. Write balanced equations for the reactions of methyl iodide with the following compounds: (a) AgOH, (b) C_2H_5ONa, (c) CH_3COOAg, (d) $AgNO_2$. To what class should these reactions be attributed from the point of view of (a) final results, (2) the character of cleavage of the C—I bond, and (3) the character of the reagent?

314. Write the general equation of the nucleophilic substitution reaction. Characterize the structure of nu-

cleophilic reagents. Give examples of nucleophiles containing carbon, nitrogen, oxygen and sulphur.

315*. Define basicity and nucleophilicity. Arrange the following anions (in each series) in the order of their increasing nucleophilic properties (toward methyl bromide in water): (a) CH_3O^-, CH_3COO^-, HO^-; (b) F^-, Br^-, I^-, Cl^-.

316. Using alkaline hydrolysis of methyl bromide, explain the essence of the S_N2 reaction. What is the geometry of the transition state? Give the energy diagram of the reaction. Specify the conditions that promote S_N2 reactions.

317*. The optically active 2-bromobutane reacts with KI in the conditions of bimolecular nucleophilic substitution reactions. Write the reaction. Describe the transition state. What is the stereochemical result of the process?

318. Arrange the following compounds in the order of their increasing reactivity in S_N2 reactions:

(a) $CH_3—CHBr—CH_3$, $CH_3—CH_2—CH_2—Br$, $(CH_3)_3C—Br$

(b) $CH_3—CHBr—CH_3$, $CH_3—CHCl—CH_3$, $CH_3—CHI—CH_3$

Explain.

319*. Explain why the rate of the reaction of ethyl bromide with KI in acetone (S_N2) is 2000 times as high as compared with the rate of the reaction of *tert*-butyl bromide in these conditions.

320. Write the reaction of ethyl bromide with an aqueous solution of alkali. How will the rate of the reaction change if (a) ethyl iodide, (b) ethyl chloride are used instead of ethyl bromide? Develop your reasons.

321. In what medium (aqueous alcoholic or alcoholic alkali) should propyl chloride be hydrolyzed? Give your reasons.

322*. How will the character of the entering group affect the rate of the S_N2 reaction? Among the anions given below, indicate (a) the strongest base, (b) the strongest nucleophile:

$$HO^-,\ Cl^-,\ RO^-,\ I^-$$

The medium is alcohol.

323*. The relative reactivity of water and acetate ion with methyl bromide is 1 : 520. How can the difference be explained? Into which direction will the ratio shift if aqueous alkali solution is substituted for water?

324*. Write the reactions of methyl bromide in an aqueous medium with the following compounds: (a) CH_3COOK, (b) KI, (c) KOH. In what case will the reaction rate be the highest and why?

325*. Write the following reactions:

(a) $n\text{-}C_4H_9Br + n\text{-}C_4H_9O^-Na^+ \longrightarrow \ldots$

(b) $n\text{-}C_4H_9Br + n\text{-}C_4H_9S^-Na^+ \longrightarrow \ldots$

Explain why the rates of these reactions (in ethyl alcohol at 25°C) relate to each other as 1 : 1800.

326*. Explain why I^- accelerates hydrolysis of primary alkyl chlorides.

327*. Compare susceptibility of methyl bromide and neopentyl bromide to S_N2 and S_N1 reactions. Explain the differences.

328. Using hydrolysis of tertiary butyl bromide with water as an example, consider the mechanism of the monomolecular nucleophilic substitution reaction. Give the energy diagram of the reaction. Consider the stereochemistry of the process. What factors promote the S_N1 reactions?

329. What is the mechanism of hydrolysis of (a) propyl iodide, (b) 2-chloro-2-methyl butane? In what conditions should each of these compounds be hydrolyzed to attain the highest yield of alcohol?

330. What mechanism of hydrolysis of *tert*-butyl chloride do the following facts prove: (a) during hydrolysis with water, the rate is proportional to the concentration of only the starting chloride, (b) as alkali is added, the rate of hydrolysis does not change?

331*. The optically active 3-bromo-3-methylhexane reacts with KI according to the S_N1 mechanism. Write the reaction. Draw the spatial structure of the intermediate compound. What is the stereochemical result of the reaction?

332. Arrange the following compounds in the order of their increasing reactivity in the S_N1 reactions:

(a) $CH_3CH_2CH_2CH_2Cl$, $CH_3—CHCl—CH_2CH_3$, $(CH_3)_3C—Cl$

(b) $(CH_3)_3C—I$, $(CH_3)_3C—Cl$, $(CH_3)_3C—Br$

Develop your reasons.

333. Explain why the rate of hydrolysis of *tert*-butyl bromide in 80 per cent ethyl alcohol at 55°C (S_N1) is 5×10^3 times higher than of isopropyl bromide.

334*. In what medium will *tert*-butyl chloride be hydrolyzed easier: (a) in aqueous alcoholic, or (b) in alcohol-ether? Develop your reasons.

335*. Choose the optimum conditions to accomplish the conversion

$$(CH_3)_3C-Br \xrightarrow{?} (CH_3)_3C-OCOCH_3$$

out of the following:

(a) CH_3COONa in alcohol, (b) CH_3COONa in water,
(c) CH_3COOH (a nucleophile and a solvent),
(d) CH_3COOH with a small quantity of water.

336. For S_N1 and S_N2 reactions, compare: (a) kinetics of the process, (b) the number of steps, (c) stereochemistry, (d) dependence of the reaction rate on the nature of the hydrocarbon radical, the character of the halogen, the character of the nucleophilic reagent, and the nature of the solvent.

337. Write the reaction of 2-bromopropane with an aqueous solution of alkali. What side product will be obtained in this reaction? Consider the mechanism of its formation.

338. Indicate the factors promoting E2 reactions. Into what direction will the ratio of products of the reaction between 2-bromopropane and alkali shift if an alcoholic solution of alkali is substituted for the aqueous solution? Develop your reasons.

339*. Compare the nucleophilic properties of ethyl alcohol and sodium ethoxide. Characterize the reaction of isopropyl bromide with each of these reagents. Write these reactions and explain their mechanism.

340*. Arrange the following compounds in the order of their increasing activity as dehydrohalogenating agents: (a) H_2O, (b) $(CH_3)_3CO^-K^+$, (c) C_2H_5OH, (d) $CH_3CH_2O^-Na^+$, (e) $(CH_3)_2CHO^-Na^+$. Develop your reasons.

341. Explain the cause of formation of a tertiary alcohol in the hydrolysis of neopentyl iodide according to this equation

$$(CH_3)_3C-CH_2I \xrightarrow{H_2O,\ Ag^+} CH_3-\underset{\displaystyle CH_3}{\overset{\displaystyle |}{C}}(OH)-CH_2CH_3$$

342. Write reactions of dehydrobromination with alcoholic solution of alkali of the following compounds:

(a) $CH_3-\underset{\displaystyle CH_3}{\overset{|}{C}}Br-CH_2CH_3$, (b) $CH_3-CH_2-CHBr-CH_2-CH_3$

(c) $CH_2Br-CH_2CH_2CH_2CH_3$, (d) $CH_3-CHBr-CH(CH_3)-CH_2CH_3$

Formulate the Zaitsev rule. Explain.

343*. 2-Bromopentane reacts with KOH in alcohol according to the E2 mechanism. Describe the transition state. Which of the possible geometric isomers of the olefin is formed?

344. What products can be formed by the action of water on *tert*-amyl chloride? Write the reactions and consider their mechanisms.

345*. 2-Bromo-2-methylbutane (I) and 2-bromo-2,4,4-trimethylpentane (II) were dehydrobrominated with potassium ethoxide in a low-polar solvent (*E*2 mechanism). The quantitative ratio of the compound (I) to the compound (II) is 0.43 in the former and 1.17 in the latter case. Explain the results.

346*. Indicate the most favourable conditions for accomplishing the following transformations:

(a) $CH_3-CHBr-CH_2-CH_3 \xrightarrow{?} CH_3-CH(OH)-CH_2-CH_3$

(b) $CH_3CH_2CH_2CH_2Br \xrightarrow{?} CH_3CH_2CH_2CH_2I$

(c) $CH_3CH_2CH_2CHBrCH_3 \xrightarrow{?} CH_3CH_2CH=CH-CH_3$

(d) $CH_3-CH(CH_3)-CHCl-CH_3 \xrightarrow{?} CH_3-CH(CH_3)-CH=CH_2$

Justify your choice in each case.

347. Using 1-bromobutane obtain the following: (a) butyl alcohol, (b) 1-butene, (c) 1-butyne, (d) butyl acetate, (e) methylbutyl ether, (f) butylamine, (g) valeronitrile.

348. Using isopropyl iodide obtain the following: (a) magnesium isopropyliodide, (b) 2,3-dimethylbutane, (c) isopropyl formate, (d) 2-nitropropane.

349. By what reactions can 1,1-dichloroethane be differentiated from 1,2-dichloroethane?

UNSATURATED HALOGEN DERIVATIVES

350. What monochloro-derivatives can be obtained from propylene? Name them.

351. Name the following compounds:

(a) $CH_3—CHCl—CH=CH_2$, (b) $CH_3—CH_2—CH=CHBr$

(c) $CH_2Br—CH=CH—CH_3$, (d) $CH_2=CH—CH_2—CH_2I$

To what type of unsaturated halogen derivatives can each of them be attributed?

352. Compare the action of chlorine on propylene at room and elevated (400°C) temperatures. Write the reactions. Consider their mechanisms.

Vinyl Halides

353. Write reactions for industrial manufacture of vinyl chloride.

354. What compound is formed by the following transformation:

$$CH_3—C\equiv CH \xrightarrow[(Hg^{2+},\ H^+)]{H_2O} \ldots \xrightarrow{PCl_5} \ldots \xrightarrow[(alcohol)]{KOH(1\ mole)} \ldots\ ?$$

355. Perchloroethylene, trichloroethylene and sym-dichloroethylene are used as incombustible solvents that do not cause corrosion. Write synthesis of these compounds on the basis of acetylene.

356. Draw the atomic-orbital diagram of the molecular structure of vinyl chloride. Characterize the reactivity of chlorine in this compound.

357*. Explain why the dipole moment of vinyl bromide ($\mu = 1.40$ D) is less than of ethyl bromide ($\mu = 1.88$ D). What is the action of these compounds to nucleophilic reagents?

358*. Write the reaction of vinyl chloride with hydrogen bromide. Explain the effect of static and dynamic factors on the direction and the rate of the reaction.

359. Write the reaction for preparing polyvinyl chloride: (a) from acetylene, (b) from 1,2-dichloroethane.

Allyl Halides

360. Obtain allyl chloride from (a) propylene and (b) allyl alcohol.

361. Write balanced equations for the reactions of N-bromosuccinimide with propylene and with 1-butene. Name the reaction products.

362. What compounds can be obtained by the following reaction:

$$CH_2=CH-CH=CH_2+HCl \longrightarrow \ldots$$

363*. Characterize the activity of allyl halides in monomolecular and bimolecular nucleophilic substitution reactions. Explain.

364. Indicate and explain which of the following compounds has normal, decreased or increased susceptibility to nucleophilic substitution reactions:

(a) $BrCH=CH-CH_3$, (b) $CH_2=CH-CH_2Br$

(c) $CH_2=CH-CH_2CH_2Br$, (d) $CH_3CH_2CH_2Br$

365*. *tert*-Chlorobutyl, and also allyl chloride were hydrolyzed in a mixture of water and acetone (1 : 1). The rate of which reaction will be higher and why?

366. By what reactions can the following compounds be differentiated?

(a) $CH_3-CH=CHCl$ and $CH_2=CH-CH_2Cl$

(b) $CH_3-CH=CH-CH_2Br$ and $CH_2=CH-CH_2-CH_2Br$

367*. Write the following reactions (in the absence of peroxides):

(a) $CH_2=CH-CH_2Cl+HBr \longrightarrow \ldots$

(b) $CH_2=CH-CCl_3+HBr \longrightarrow \ldots$

Consider the mechanism of the reactions.

368*. Obtain (a) $CH_3CHBrCH_2Cl$, and (b) $CH_2BrCH_2CH_2Cl$ from propylene via allyl chloride.

369*. Predict the result of the successive reactions:

$$CH_2=CH-CH_2Br \xrightarrow{Br_2} \ldots \xrightarrow[(alcohol)]{NaOH(1\ mole)} \ldots \xrightarrow{C_2H_5MgBr} \ldots$$

370. Synthesize the compounds given below from allyl bromide:

(a) $CH_3-CH(CH_3)-CH_2-CH=CH_2$

(b) $CH_2=CH-CH_2-CH_2-CH=CH_2$

(c) $CH_2Br-CHBr-CH_2Br$

371*. As crotyl bromide, $CH_3CH=CHCH_2Br$, is heated for five minutes at a temperature of 100°C, an equilibrium mixture of 85 per cent of the original compound and 15 per cent of its isomer is formed. What is the structure of the isomer? What is the mechanism of the isomerization?

372*. 3-Chloro-1-butene is hydrolyzed to give two isomeric alcohols. Write the reaction and consider its mechanism.

373*. What products are formed in the reaction?

$$CH_2=C(CH_3)-CH(CH_3)-Cl \xrightarrow[S_N1]{CH_3OH} \ldots$$

Explain.

Fluorine Derivatives

374. Explain why fluorine reacts with saturated hydrocarbons to give low yields of its derivatives.

375*. What reactions can be used to prepare the following compounds: (a) perfluoroheptane, (b) perfluoroethylene, (c) isopropyl fluoride?

376. Accomplish the following transformations:

$$CH_4 \rightarrow \begin{cases} CFCl_3 \\ CF_2Cl_2 \\ F_2C=CF_2 \end{cases}$$

Indicate practical uses of the obtained compounds.

377. Characterize the length, energy, polarity and polarizability of the C—F bond. Compare it with other carbon-halogen bonds. Compare the reactivity of CH_3-F, CH_3-Cl, CH_3-Br and CH_3-I in nucleophilic substitution reactions.

378*. Explain why the compounds CH_3CHF_2 and CH_3CF_3 are inactive toward nucleophilic reagents.

379. Write the reaction of preparing fluoroplastic Teflon. Characterize the properties of this polymer. Explain the

high stability of perfluorohydrocarbons to the action of chemical reagents.

380. Give examples of fluorinated compounds used as: (a) monomers, (b) solvents, (c) refrigerants.

D. Establishing the Structure of Organic Compounds by Their Properties

381. Write the structural formula of a substance having the composition of C_4H_9Br that gives a primary alcohol on hydrolysis, and a tertiary bromine derivative on dehydrobromination and subsequent hydrobromination.

382. The substance C_4H_9Br reacts with sodium on heating to give 3,4-dimethylhexane. What is the structure of the original compound?

383. Write the structural formula of the compound $C_5H_{11}Cl$, giving the product $C_5H_{12}O$ on its hydrolysis. The latter gives a mixture of formaldehyde and methyl ethyl ketone on its dehydration and further ozonolysis.

384. The compound $C_5H_{11}Br$ undergoes dehydrobromination and then ozonolysis to give a mixture of formaldehyde and isobutyric aldehyde. What is the structure of the original substance?

385. Write the structural formula of the compound $C_5H_{10}Br_2$ that forms methyl propyl ketone on its hydrolysis. Obtain $C_5H_{10}Br_2$ from 1-pentyne.

386*. Establish the structural formula of the compound $C_6H_{12}Cl_2$ that is hydrolyzed into a carbonyl compound. The latter does not give the iodoform reaction and is oxidized into a mixture of acetic, propionic, and butyric acids.

387. What is the structural formula of a bromine derivative having the composition C_3H_5Br? It does not enter nucleophilic substitution reactions and is hydrobrominated into 2,2-dibromopropane.

388*. The compound C_4H_7Br can be obtained by the action of N-bromosuccinimide on 1-butene. C_4H_7Br is hydrolysed to give a mixture of two isomeric products having the composition C_4H_8O. Write structural formulas of C_4H_7Br and C_4H_8O, equations of the reactions, and consider their mechanisms.

389*. Establish the structure of the compound $C_2H_3Cl_3$ by its NMR spectrum (Fig. 4).

390*. The NMR spectrum of the compound $C_3H_3Cl_5$ has the following signals: δ_1 4.52 ppm (triplet) and δ_2 6.07 ppm

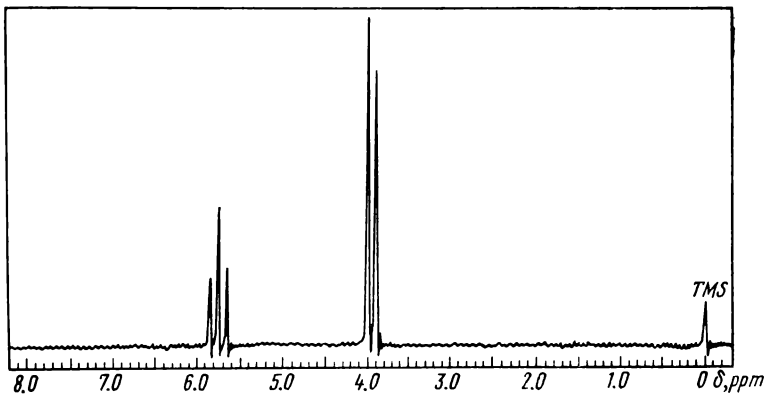


Fig. 4. NMR spectrum of $C_2H_3Cl_3$

(doublet). What conclusion concerning the structure of the compound can be made?

391*. Establish the structure of the compound $C_4H_4Cl_2$ by the following spectral data: (a) its NMR spectrum has one signal at δ 4.2 ppm (singlet); (b) the compound does not absorb in the region of 200-380 nm of the U-V spectrum.

CHAPTER SIX

ORGANOMETALLIC COMPOUNDS. ORGANOSILICON AND ORGANOPHOSPHORUS COMPOUNDS

ORGANOMETALLIC COMPOUNDS

392. Name the following compounds: (a) C_2H_5ONa, (b) CH_3MgBr, (c) CH_3CH_2COONa, (d) $Hg(CH_3)_2$, (e) $CH_3CH_2CH_2CH_2Li$, (f) $CH_3—C\equiv C—Na$. Which of them are organometallic compounds?

393. Write structural formulas of the following compounds: (a) diethylzinc, (b) vinyllithium, (c) methylcadmium chloride, (d) methyltin trichloride, (e) tetraethyllead.

394. Consider the character of the carbon-metal bond in the following organometallic compounds: CH_3Na, $Pb(C_2H_5)_4$, C_2H_5MgBr, $Zn(CH_3)_2$, $Hg(C_2H_5)_2$. Arrange these compounds in the order of their increasing reactivity toward water.

395. Use ethyl bromide to obtain: (a) ethyllithium, (b) diethylzinc, (c) diethylmercury.

396. Use diethylmercury to obtain: (a) ethylsodium, (b) diethylmagnesium, (c) diethylzinc.

397*. Indicate and explain which of the following reactions can be accomplished:

(a) $(CH_3)_2Zn + Cd \longrightarrow \ldots$

(b) $(C_2H_5)_4Pb + Zn \longrightarrow \ldots$

(c) $(C_2H_5)_2Mg + Hg \longrightarrow \ldots$

(d) $(C_2H_5)_2Mg + Li \longrightarrow \ldots$

Name the starting and final compounds.

398. Obtain butyllithium from butyl bromide. Write balanced equations for the reactions of butyllithium with (a) H_2O, (b) HCl, (c) CH_3COCH_3, (d) CO_2. What accounts for the wide use of organolithium compounds in organic synthesis?

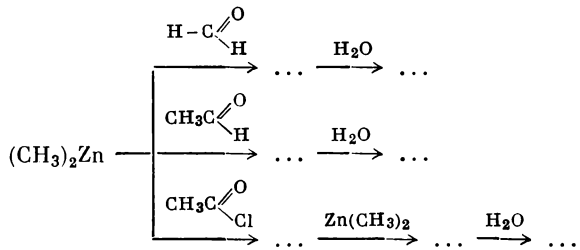
399. What compound is formed by the action of sodium on diethylmercury? Characterize the chemical properties of organosodium compounds. Why is it impossible to obtain

organosodium compounds by the action of sodium on halogen derivatives?

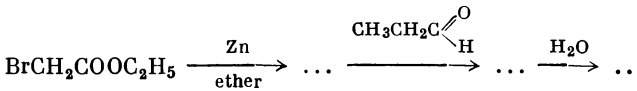
400. Write reactions for preparing the following organosodium compounds: (a) amylsodium, (b) sodium vinylacetylide. How do these compounds react with water?

401. Obtain diethylzinc: (a) from the corresponding alkyl halide, (b) from another organometallic compound. What accounts for the ability of the obtained compound to be distilled (in an inert gas)?

402. Write the following reactions:



403*. Complete the following:



404. By whom and when were mixed organomagnesium compounds introduced into laboratory practice? Write reactions for preparing ethylmagnesium iodide and propylmagnesium bromide. Specify the conditions of the reactions. What is the role played by absolute ether in this reaction?

405. Arrange the following halogen derivatives in the order of their decreasing activity toward magnesium: (a) $CH_3CH_2CH_2Cl$, (b) $CH_3CH_2CH_2I$, (c) $CH_3CH_2CH_2Br$. Develop your reasons.

406*. Even heating in vacuum fails to remove all ether from the Grignard reagent. Explain.

407. Organomagnesium compounds should be prepared in inert gas atmosphere since it precludes the reaction of the Grignard reagent with moisture, oxygen, and CO_2 of the air. How does the Grignard reagent react with these compounds?

408. Write the reaction of ethylmagnesium bromide with allyl bromide. Compare the character of polarization of the carbon-metal and carbon-halogen bonds in the original substances. What type of substitution is the reaction with: (a) alkyl halide, (b) Grignard reagent?

409. Write the reactions of ethylmagnesium bromide with compounds containing active hydrogen atoms: (a) water, (b) propyl alcohol, (c) ammonia, (d) ethylamine, (e) acetylene.

410. Why cannot sulphuric ether, used for preparing the Grignard reagent, contain admixtures of water or alcohol?

411. Determine percentage content of hexyl alcohol in its mixture with hexane, if 11.2 cc of methane are obtained from 0.2020 g of the sample during determination of active hydrogen by the Chugaev-Zerevitinov method.

412. Determine the content of active hydrogen in a test substance from the following data: a sample weighing 0.1760 g yields 14.8 cc of methane (0°C, 760 mm Hg).

413*. Complete the following equations:

(a) $CH_3CH_2CH_2MgI + (CH_3)_2SO_4 \longrightarrow \ldots$

(b) $CH_3CH_2MgBr + CH_3C{\equiv}C{-}CH_2Br \longrightarrow \ldots$

(c) $CH_3CH_2CH_2MgBr + ClCH_2OCH_3 \longrightarrow \ldots$

414*. What compound is formed by the action of iodine on propylmagnesium bromide?

415. Write the reactions in which propylmagnesium iodide and butylmagnesium iodide are oxidized by atmospheric oxygen. What products are formed in hydrolysis of the obtained compounds?

416. What compounds are formed by the reaction of propylmagnesium iodide with formaldehyde, with propionic aldehyde, with methyl ethyl ketone? Write balanced equations for the reaction of hydrolysis of the obtained products.

417. Using the Grignard reaction, obtain the following: (a) 1-hexanol, (b) 2-butanol, (c) triethylcarbinol.

418. Write the reaction between butylmagnesium bromide and ethylene oxide.

419. Using propyl bromide, obtain 1-pentanol by the Grignard reaction.

420. Obtain methyldiethylcarbinol (1) from a carbonyl compound, (2) from carboxylate ester.

421*. In what conditions can mixed organomagnesium compounds be obtained from vinyl halides? Obtain vinylmagnesium bromide by the Normant reaction.

422. Obtain the following organomagnesium compounds from the corresponding acetylene hydrocarbons: $CH_3CH_2C{\equiv}CMgBr$, $(CH_3)_2CH{-}C{\equiv}CMgBr$.

423. Write the synthesis of ethynylcarbinol and methylethynylcarbinol from acetylene.

424*. Obtain isopropyl alcohol from ethyl formate and the corresponding Grignard reagent.

425*. Write the reaction for preparing methyl ethyl ketone from acetyl chloride by the Grignard reaction. Why are the best results in this reaction obtained with the mixed organocadmium compound?

426. Complete the following:

$$CH_3C{\equiv}N + C_2H_5MgBr \longrightarrow \ldots \xrightarrow{2H_2O} \ldots$$

427. Obtain valeric acid from butylmagnesium bromide.

428. Write the reaction of preparing acetylenecarboxylic acid from acetylene.

429*. Explain why the Grignard reagent is easy to add to a carbonyl group, but it does not react with the double bond of ethylene hydrocarbons.

430*. 3-Pentene-2-one reacts with ethylmagnesium bromide (molar ratio 1 : 1), with subsequent hydrolysis, to give a mixture of two compounds:

(a) $CH_3CH_2CH(CH_3)CH_2COCH_3$, (b) $CH_3CH{=}CH{-}\underset{\displaystyle CH_3}{\underset{|}{C}}(OH){-}CH_2CH$

Explain the results.

431*. What is the structure of the insecticide granosan obtained by the following reaction?

$$2C_2H_5Cl \xrightarrow{2Na-Hg} \ldots \xrightarrow{HgCl_2} \ldots$$

432. Describe the industrial method of manufacturing tetraethyllead. Indicate its practical uses.

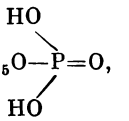
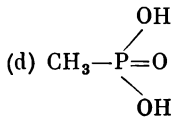
433. What is the role of organolead compounds in the study of free aliphatic radicals?

ORGANOSILICON AND ORGANOPHOSPHORUS COMPOUNDS

434. What compounds can be obtained by the reaction of tetrachlorosilane with CH_3MgI? Name them.

435. What methods are used in industry for the manufacture of organosilicon compounds? Write the reactions for preparing dimethyldichlorosilane and its conversion into silicone.

436. Name the following compounds:

(a) $(CH_3)_3P$, (b) $(C_2H_5O)_3P$, (c)  , (d) 

437. Obtain diethyl propylphosphonate from triethyl phosphite (the Arbuzov reaction).

438. Obtain 3-methyl-2-pentene by the Wittig reaction.

CHAPTER SEVEN

MONOHYDRIC AND POLYHYDRIC ALCOHOLS

A. Isomerism. Nomenclature

439. Write structural formulas of all isomeric alcohols having the composition C_3H_7OH and C_4H_9OH. Give their rational and IUPAC names. Indicate primary, secondary and tertiary alcohols.

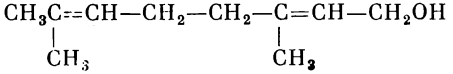
440. Write structural formulas of all saturated monohydric secondary alcohols of normal structure containing 3, 4, 5, and 6 carbon atoms. Give their carbinol names.

441. How many tertiary alcohols have the molecular formula $C_6H_{14}O$, $C_7H_{16}O$? Write their structural formulas and give their IUPAC names.

442. Give carbinol names to the following alcohols: (a) $(CH_3)_2CH-CH_2OH$, (b) $(CH_3)_3C-CH(OH)-CH_3$, (c) $(CH_3)_3C(OH)$.

443. Write structural formulas and give IUPAC names to unsaturated alcohols: allyl, propargyl, and vinylethylcarbinol.

444*. Give IUPAC name to the unsaturated alcohol:



How many compounds have the same structural formula?

445. Write structural formulas of all isomeric dihydric alcohols having the molecular formula $C_4H_{10}O_2$. Name them.

446. Give IUPAC names to the following alcohols:

(a) $CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH(OH)-CH_3$, (b) $(OH)CH_2-CH_2(OH)$

(c) $CH_3-CH=CH-CH_2OH$

(d) $CH_3-\underset{\displaystyle CH_3}{\underset{|}{C}}(OH)-\underset{\displaystyle CH_3}{\underset{|}{C}}(OH)-CH_3$

(e) $(CH_3)_2CH-CH_2-CH(OH)-CH_2OH$

(f) $CH_3-CH(OH)-CH=CH_2$, (g) $(OH)CH_2-CH(OH)-CH_2OH$

(h) $HO-CH_2-C\equiv C-CH_2OH$, (i) $CH_3-\underset{\displaystyle CH_3}{\underset{|}{C}}(OH)-C\equiv CH$

447. Write structural formulas of the following compounds: 2-methyl-1-pentene-3-ol; 1,3-butanediol; trimethylene glycol.

B. Methods of Preparing

448. What alcohols are formed by alkaline hydrolysis of (a) ethyl bromide, (b) isopropyl iodide, (c) isobutyl chloride? Write the reactions, and consider their mechanisms.

449. *tert*-Chlorobutyl forms, in an aqueous-alcoholic medium, *tert*-butyl alcohol and a small quantity of isobutylene. Boiling of this halogen derivative in an aqueous-alcoholic solution of alkali gives only isobutylene. Explain.

450. What alcohols are formed by the alkaline hydrolysis of 1,4-dibromobutane, ethylene chlorohydrin?

451. Write the hydration of propylene in the presence of sulphuric acid. Consider the mechanism of the reaction.

452. By hydration of what ethylene hydrocarbons can the following alcohols be obtained: (a) 2-methyl-2-butanol, (b) 3-pentanol, (c) 2,3-dimethyl-2-butanol?

453. Why does the rate of hydration of alkenes in an acid homogeneous catalysis increase in the following series?

$$\text{ethylene} < \text{propylene} < \text{isobutylene}$$

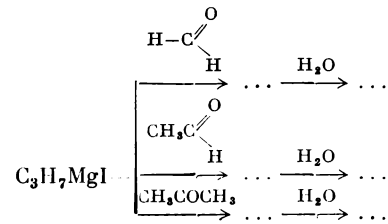
454. What hydrocarbon is easy to hydrate in the presence of sulphuric acid: trimethylethylene or isopropylethylene? Write the reactions and explain them.

455. Technical *sec*-amyl alcohol is a mixture of alcohols obtained by hydration of a mixture of 1-pentene and 2-pentene with sulphuric acid. What is the structure of the alcohols that are constituents of technical *sec*-amyl alcohol?

456. Suggest the way to accomplish the following conversion:

$$(CH_3)_2CH—CH_2OH \rightarrow (CH_3)_3C—OH$$

457. What alcohols are formed by the following reactions?



458. Use propylmagnesium bromide to obtain the following primary alcohols: (a) propyl, (b) *n*-butyl, (c) *n*-amyl.

459. Using the Grignard reaction, synthesize secondary alcohols: (a) methylpropylcarbinol, from the corresponding aldehyde, (b) dibutylcarbinol, from ethyl formate and butyl bromide.

460. What carbonyl components should be used to synthesize: (a) dimethylethylcarbinol, (b) methyldiethylcarbinol from ethylmagnesium bromide?

461. Write the reaction of preparing triisopropylcarbinol from isopropyllithium and the corresponding carbonyl compound.

462. Suggest a method for preparing diethylpropylcarbinol from ethylmagnesium bromide, using: (a) a corresponding carbonyl compound, (b) an ester.

463*. Which of the following alcohols can be obtained by the Grignard reaction from carboxylate esters:

(a) $(CH_3)_3C-OH$, (b) $CH_3-\underset{\displaystyle C_2H_5}{\overset{\displaystyle C_2H_5}{\underset{|}{\overset{|}{C}}}}-OH$, (c) $CH_3-\underset{\displaystyle C_3H_7}{\overset{\displaystyle C_2H_5}{\underset{|}{\overset{|}{C}}}}-OH$

Write equations for their synthesis.

464. Use the Grignard reaction to obtain tertiary alcohols having, at the OH-group bonded carbon: (a) three similar radicals, (b) three different radicals, (c) two similar radicals.

465. Convert propylene into dimethylisopropylcarbinol using only inorganic reagents.

466. What monohydric alcohols can be obtained by reducing the following carbonyl compounds:

(a) $CH_3-CH(CH_3)-CHO$, (b) $C_2H_5-CO-C_2H_5$, (c) $CH_3-CO-C_3H_7$

What reducing agents are required to realize these conversions?

467. Obtain the following alcohols:

(a) $CH_3CH_2—CH(OH)—CH_2—CH(CH_3)—CH_3$

(b) $CH_3—CH(OH)—CH(OH)—CH_3$

(c) $CH_3—CH(CH_3)—CH_2CH_2OH$, (d) $(OH)CH_2—CH_2—CH_2(OH)$

by reducing the corresponding carbonyl compounds.

468. Write the reaction of preparing pinacol from acetone. Consider the mechanism of the reaction.

469. What compounds are formed from dipropylketone by its reduction with: (a) hydrogen in the presence of Raney nickel, (b) magnesium amalgam? Write balanced equations and name the obtained compounds.

470*. What compounds are formed by the following reactions?

(a) $CH_3(CH_2)_{10}COOC_2H_5 \xrightarrow{LiAlH_4} \ldots \xrightarrow{H_2O} \ldots$

(b) $CH_3(CH_2)_7—CH=CH(CH_2)_7—COOC_4H_9 \xrightarrow{C_2H_5OH+Na} \ldots \xrightarrow{H_2O} \ldots$

(c) $H_5C_2OOC—(CH_2)_4—COOC_2H_5 \xrightarrow[\text{copper-chromium catalyst}]{H_2} \ldots$

Name them.

471. Write balanced equations of reactions underlying commercial methods for preparing methyl, ethyl, and isopropyl alcohols.

472. Using alcohols containing not more than four carbon atoms, obtain 2-methyl-1-butanol and 4-methyl-1-pentanol. Write the reactions.

473. Obtain allyl alcohol from propylene. Describe the mechanism of the reactions.

474*. Using propylene, prepare the following alcohols: (a) 4-pentene-2-ol, (b) 2-methyl-4-pentene-2-ol.

475. Write the reaction of preparing propargyl alcohol by ethynylation of formaldehyde. Consider the mechanism of the reaction.

476. Using acetylene and the corresponding carbonyl compounds, obtain the following: (a) butynediol, (b) dimethylethynylcarbinol. What are the practical uses of these alcohols?

477. Complete the following:

(a) $CH_2=CH_2 \xrightarrow{Br_2} \ldots \xrightarrow[(CH_3COOH)]{CH_3COOK} \ldots \xrightarrow[(H+)]{H-OH} \ldots$

(b) $CH_2=CH_2 \xrightarrow[(Ag,\ heat)]{O_2} \ldots \xrightarrow[(H+)]{H-OH} \ldots$

478. Give an example of preparing α-glycol by oxidation of olefin with potassium permanganate. What are the required reaction conditions?

479. Write balanced equations of the reactions used for commercial manufacture of glycerol: (a) by saponification of fats, (b) from propylene, (c) from acetylene.

C. Structure and Properties of Monohydric Alcohols

480. Draw the structure of the outer electron shell of the oxygen atom and characterize its covalence.

481. Draw the atomic-orbital model of a molecule of methyl alcohol. Give the general characteristics of the C—O and O—H bonds. Characterize the reactivity of alcohols from the aspect of these data.

482. Explain why methyl alcohol (b.p. 64.7°C) boils at temperatures much higher than methyl fluoride (b.p. —78.2°C), or ethane (b.p. —88.6°C), although their molecular masses are quite comparable. What accounts for the high solubility of lower alcohols in water?

483. What is the hydrogen bond? What type of hydrogen bonding is characteristic of alcohols? What properties of alcohols depend on the presence of the hydrogen bond?

484. Characterize the I-R spectra of saturated alcohols.

485. Explain why the I-R spectrum of ethyl alcohol (in the gaseous phase) has a sharp absorption band at 3700 cm^{-1}, while the spectrum of 10% ethyl alcohol in CCl_4 has a wide absorption band at 3350 cm^{-1}.

486. Consider the I-R spectrum of *tert*-butyl alcohol (liquid film, Fig. 5) and identify absorption bands due to valence and deformational oscillations of separate groups of atoms.

487. The I-R absorption spectrum of isopropyl alcohol has the following absorption bands (cm^{-1}): 950 (s), 1150 (s), 1365 (m), 1380 (m), 1460 (m), 2880, 2930, 2962 (s), 3440 (s, wd)*. Oscillation of what groups of atoms do they show?

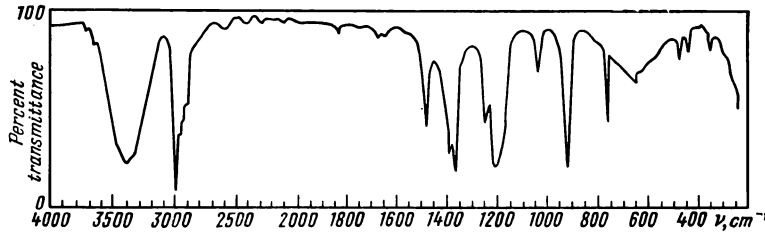


Fig. 5. I-R spectrum of tertiary butyl alcohol

488. Analyze the NMR spectrum of ethyl alcohol (Fig. 6). Indicate the quantity and type of protons corresponding to the resonance signals available.

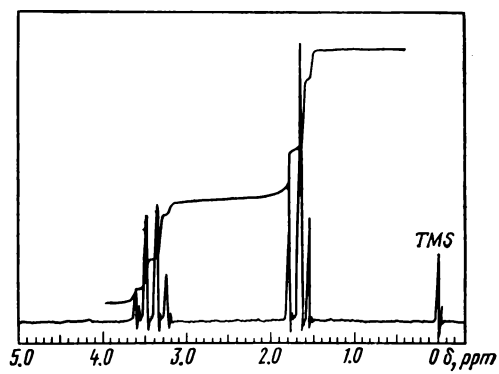


Fig. 6. NMR spectrum of ethyl alcohol

489. Write reactions characterizing acid and basic properties of alcohols. What are oxonium compounds?

490. Write a balanced equation of autoprotolysis of water, ethyl alcohol. Explain why ethyl alcohol is a weaker acid ($pK_a = 18$) compared with water ($pK_a = 14$).

* Abbreviations 's', 'm' and 'wd' stand for 'strong', 'medium', and 'wide', respectively.

491. Arrange the following alcohols in the order of their decreasing acid properties: methyl alcohol, *tert*-butyl alcohol, isopropyl alcohol. Develop your reasons.

492. Write a balanced equation for the reaction of ethyl alcohol with sodium metal. Characterize basic properties of the alcohol and nucleophilic properties of ethoxide anion.

493. Write a balanced equation of the reaction used for commercial manufacture of sodium ethoxide. Specify the reaction conditions.

494*. Why do alkyl halides easily enter nucleophilic substitution reactions, whereas alcohols do it only in the presence of catalysts (strong acids)?

495. Write a balanced equation for the reaction of ethyl alcohol with potassium bromide in the presence of sulphuric acid with heating. Compare the mechanism of this reaction with that of alkaline hydrolysis of ethyl chloride.

496. Write balanced equations for reactions of propyl alcohol and *tert*-butyl alcohol with hydrobromic acid. Consider the mechanisms of the reactions and explain the differences.

497*. Ethyl alcohol easily reacts with hydrobromic acid to give ethyl bromide, whereas ethyl chloride is formed only with saturation of the alcohol with dry HCl, or with heating in a sealed vessel. Explain.

498. Write balanced equations of reactions of *n*-propyl alcohol with PCl_3, PCl_5 and $SOCl_2$. Consider the mechanism of the second reaction.

499*. Write the reaction for preparing 2-iodooctane from 2-octanol, iodine, and red phosphorus. What is the advantage of this method over the method of preparing iodine derivatives from an alcohol and HI?

500. Write esterification of acetic acid with ethyl alcohol in the presence of sulphuric acid. Consider the mechanism of the reaction. Indicate other catalysts used in esterification reactions.

501*. Arrange the following alcohols in the order of their increasing susceptibility to esterification with acetic acid: methyl alcohol, *tert*-butyl alcohol, isopropyl alcohol. Develop your reasons.

502. Write balanced equations for reactions of intermolecular and intramolecular dehydration of ethyl alcohol in the

presence of sulphuric acid. Specify the reaction conditions. Name the compounds formed.

503. What compounds can be obtained by the reaction of propyl alcohol with sulphuric acid in various conditions?

504. What ethylene hydrocarbons are formed during dehydration of the following alcohols?

(a) $CH_3CH_2CH_2OH$, (b) $CH_3CH(OH)CH_3$

(c) $CH_3CH(OH)CH_2CH_3$, (d) $(CH_3)_3C(OH)$

(e) $CH_3-\underset{\displaystyle CH_3}{\overset{\displaystyle |}{C}}(OH)-CH_2CH_2CH_3$, (f) $CH_3-\underset{\displaystyle CH_3}{\overset{\displaystyle |}{C}}(OH)-\underset{\displaystyle CH_3}{\overset{\displaystyle |}{C}}(OH)-CH_3$

505. Write dehydration of butyl, *sec*-butyl and *tert*-butyl alcohols in the presence of sulphuric acid. Consider the mechanisms of the reactions. Arrange the alcohols in the order of their increasing susceptibility to dehydration. Develop your reasons.

506. Specify the conditions for accomplishing the following transformations:

$$CH_3CH_2CH_2OH \longrightarrow CH_3CH(OH)CH_3$$

$$(C_2H_5)_2CH-CH_2OH \longrightarrow (C_2H_5)_2C(OH)-CH_3$$

507*. Explain why dehydrochlorination of butyl chloride with alcoholic solution of alkali gives 1-butene, whereas dehydration of *n*-butyl alcohol with sulphuric acid gives a mixture of 1-butene and 2-butene.

508. What compounds can be obtained by oxidation of the following alcohols?

(a) $CH_3CH_2CH_2OH$, (b) $CH_3-CH(OH)-CH_3$

(c) $CH_3CH_2-CH(CH_3)-CH_2OH$

(d) $(CH_3)_3C-CH_2CH_2OH$, (e) $(CH_3)_2CH-CH(OH)-CH(CH_3)-CH_3$

What is the attitude of tertiary alcohols to oxidation?

509. Write a balanced equation for the reaction of oxidation of ethyl alcohol to acetaldehyde with sodium dichromate in sulphuric acid. Calculate the necessary (theoretical) number of grams of the oxidizing agent and sulphuric acid to obtain 50 g of the aldehyde.

510. By what reactions can the isomers of butyl alcohol be differentiated?

511. Write dehydration of propyl alcohol isomers. Specify the conditions.

512. Indicate the methods for quantitative determination of primary, secondary, and tertiary alcohols. Write the corresponding reactions.

513. What is the essence of the Chugaev-Zerevitinov method for quantitative determination of active hydrogen?

514. Determine the molecular mass of a monohydric alcohol the acetylation of which (0.88 g) requires 1.03 g of acetic anhydride.

515. Determine the molecular mass of a monohydric tertiary alcohol the dehydration of 28.8 g of which gives 3.6 g of water.

516. What compounds exist in normal conditions in the form of an alcohol, a ketone: (a) $CH_2=CH-CH_2OH$, (b) $CH_2=C(OH)-CH_3$, (c) $CH_3CH=C(OH)-CH_2CH_3$? Formulate the Eltekov-Erlenmeyer rule.

517*. Knowing the values of bond energy (see Appendix, Table 1), calculate heats of formation of vinyl alcohol and acetaldehyde from atoms, and show that the equilibrium $CH_2=CHOH \rightleftharpoons CH_3-CHO$ is practically completely shifted to the right.

518. Write reactions for preparing the following derivatives of vinyl alcohol: vinyl ethyl ether, vinyl acetate. What are practical uses of these compounds?

519. What is polyvinyl alcohol? Write the reaction by which it is obtained. Describe its properties.

520. Write the reaction of allyl alcohol with: (a) hydrogen in the presence of nickel, (b) with aqueous solution of potassium permanganate, (c) with bromine water.

521*. Which of the two alcohols: (a) $CH_2=CH-CH_2OH$ or (b) $CH_2=CH-CH_2CH_2OH$ is easier to react with concentrated hydrochloric acid in the presence of $ZnCl_2$ (the S_N1 mechanism)? Develop your reasons.

522*. Explain the difference in the course of the following nucleophilic substitution reactions:

(a) $CH_2=CH-CH_2CH_2OH + HBr \longrightarrow CH_2=CH-CH_2CH_2Br$

(b) $CH_3CH=CH-CH_2OH + HBr \longrightarrow \begin{cases} CH_3CH=CH-CH_2Br\ (85\%) \\ CH_3-CHBr-CH=CH_2\ (15\%) \end{cases}$

523. Characterize chemical properties of propargyl alcohol. Write its reactions with (a) Na, (b) CH_3MgI, (c) bromine water, (d) hydrobromic acid.

D. Properties of Polyhydric Alcohols

524. Does the simplest dihydric alcohol—methylene glycol—exist? Give examples of stable glycols containing two hydroxyls at one carbon atom.

525. Explain the cause of sharp elevation of the boiling point in the transition from ethyl alcohol (+78°C) to ethylene glycol (197.5°C) and glycerol (290°C).

526. Write reactions for obtaining the following derivatives of ethylene glycol: (a) dimethyl ether, (b) monoacetate, (c) dinitrate, (d) ethylene chlorohydrin.

527. What products are formed by oxidation of ethylene glycol, glycerol?

528*. Write the reaction of oxidation of 2,3-butanediol with periodic acid. What is the practical importance of this reaction?

529. What compounds are formed: (a) by dehydration of 1,4-butanediol, (b) by dehydration of pinacol in conditions of heterogeneous catalysis (Al_2O_3)?

530*. What compound is formed by heating pinacol with dilute sulphuric acid? Give the mechanism of the reaction.

531. Complete the following:

$$CH_3CH_2CH{=}CH_2 \xrightarrow[(H^+)]{H_2O} \ldots \xrightarrow{Cu,\,300^\circ C} \ldots \xrightarrow[(Mg-Hg)]{2[H]} \ldots \xrightarrow[heat]{H_2SO_4} \ldots$$

532. Write reactions for preparing: (a) glycerol trinitrate, (b) pentaerythrite tetranitrate. What are practical uses of these compounds?

533*. Isobutyric aldehyde is produced commercially as this:

$$CH_2{=}C(CH_3)_2 \xrightarrow[20^\circ]{Cl_2} \ldots \xrightarrow[[Ca(OH)_2]]{H_2O} \ldots \xrightarrow[heat]{H^+} CH_3{-}CH(CH_3){-}C\overset{O}{\underset{H}{<}}$$

Complete the equations and consider the mechanism of the last step

534. What class of compounds are fats? What products are formed by hydrolysing them (with water, alkali)?

535*. What reactions should be used to distinguish between the following isomers:

$HOCH_2—CH(CH_3)—CH_2—CH_2—CH(CH_3)—CH_2OH$ (I)

$HOCH_2—CH_2—CH(CH_3)—CH(CH_3)—CH_2—CH_2OH$ (II)

536. Suggest reactions by which the following isomers given in pairs can be distinguished:

(a) $(CH_3)_2C(OH)—CH_2CH_3$ and $CH_3—CH(CH_3)—CH_2—CH_2OH$

(b) $CH_2=CH—CH_2CH_2OH$ and $CH_3—CH=CH—CH_2OH$

(c) $(OH)CH_2—CH_2—CH_2—CH_2(OH)$ and $CH_3—CH(OH)—CH(OH)—CH_3$

E. Establishing the Structure of Organic Compounds by Their Properties

537. Write a structural formula of the compound $C_4H_{10}O$ that reacts with sodium metal to liberate hydrogen and on oxidation forms a ketone.

538. Two amyl alcohols (I) and (II) react with PI_3 to give the corresponding monoiodine derivatives. Dehydroiodination of the latter gives the same olefin 2-methyl-2-butene. Write structural formulas of alcohols (I) and (II).

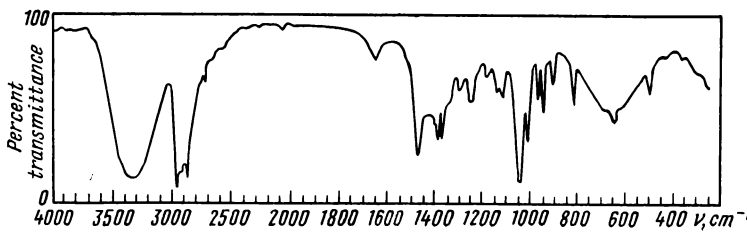


Fig. 7. I-R spectrum of $C_4H_{10}O$

539. Determine the structure of a hydrocarbon having the composition C_5H_{10}, the catalytic hydrogenation of which gives methylbutane, and whose hydrobromination (in the absence of peroxides) with subsequent hydrolysis gives an alcohol which is converted into a ketone by oxidation.

540*. What conjectures concerning the structure of the compound $C_4H_{10}O$ can be made from its I-R spectrum (liquid film, Fig. 7)?

541. What is the structure of the compound C_4H_8O that decolourizes bromine water, reacts with sodium metal to liberate hydrogen, and forms vinylacetic aldehyde by careful oxidation?

542*. Establish the structure of a compound having the composition $C_8H_{18}O_2$ and possessing the following properties: (1) reacts with methylmagnesium iodide with liberation of two moles of methane, (2) when oxidized with periodic acid it forms only methyl ethyl ketone.

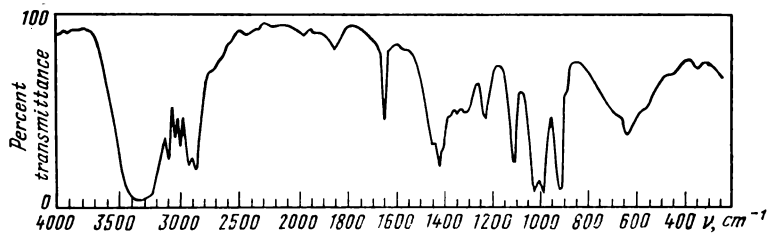


Fig. 8. I-R spectrum of C_3H_6O

543. Write a possible structural formula of the compound $C_7H_{16}O$, having the following properties: (1) when acted upon with CH_3MgI it liberates methane, (2) it is dehydrated into the hydrocarbon C_7H_{14} that gives a mixture of acetic and isovaleric aldehydes on ozonolysis.

544*. Write possible structural formulas of compounds having the formula $C_5H_{10}O$ that react with CH_3MgI to liberate methane, form $C_5H_{10}Br_2O$ with bromine, and are dehydrated to give isoprene.

545*. Establish the structure of the compound C_3H_6O from its I-R spectrum (liquid film, Fig. 8).

546*. Establish the structure of the compound C_3H_8O from the following: (1) the I-R spectrum has a wide band of absorption at 3500-3200 cm^{-1}, (2) NMR spectrum has the signals: δ_1 1.20 ppm (doublet), δ_2 1.60 ppm (singlet), and δ_3 4.00 ppm (multiplet).

CHAPTER EIGHT

ETHERS. THIOALCOHOLS. THIOETHERS

ETHERS

A. Isomerism. Nomenclature. Methods of Preparing

547. Write structural formulas of ethers having the composition $C_4H_{10}O$. Name them.

548. Name the following compounds:

(a) $C_2H_5-O-C_2H_5$, (b) $CH_3-O-CH_2CH_2CH_3$, (c) $CH_2(OCH_3)-CH_2(OCH_3)$

(d) $CH_3-CH(CH_3)-O-CH(CH_3)-CH_3$, (e) $CH_3-CH(O)-CH_2$,

(f) $CH_3-O-CH=CH_2$

549. Write structural formulas of the following compounds: (a) 1-methoxypentane, (b) monoethyl ether of ethylene glycol, (c) sym-dimethylethylene oxide.

550. Write reactions for preparing ethyl ether from ethyl alcohol in the presence of sulphuric acid. Consider the mechanism of the reaction. Define the limits of the use of the method for preparing ethers.

551*. What side process occurs alongside with the process for preparing ethers by acid dehydration of alcohols? Which ethers of those given below can be obtained by this method?

(a) CH_3-O-CH_3, (b) $CH_3(CH_2)_4-O-(CH_2)_4CH_3$

(c) $(CH_3)_2CH-O-CH(CH_3)_2$, (d) $(CH_3)_3C-O-C(CH_3)_3$

552. Prepare ethyl propyl ether by Williamson method. Consider the mechanism of the reaction.

553*. Write all possible variants of synthesis of methyl isopropyl ether according to Williamson. Which of them gives the highest yield? Develop your reasons.

554*. Write formulas of the main products obtained in the following reactions:

(a) $CH_3CH_2CH_2CH_2Br + CH_3CH_2O^-Na^+ \xrightarrow[\text{heat}]{(C_2H_5OH)} \ldots$

(b) $(CH_3)_3CBr + CH_3CH_2O^-Na^+ \xrightarrow[\text{heat}]{(C_2H_5OH)} \ldots$

Explain the differences in the course of the reactions.

555*. Explain which of the reactions below should reasonably be used for preparing di-*tert*-butyl ether: (1) dehydration of *tert*-butyl alcohol in the presence of sulphuric acid, (2) action of *tert*-butyl chloride on *tert*-butyl alkoxide, (3) action of silver oxide on *tert*-butyl iodide.

556. Using acetylene obtain the following: (a) methyl vinyl ether, (b) butyl vinyl ether. Specify the reaction conditions. Describe the mechanism of the reactions.

557*. Complete the following:

$$2HOCH_2—CH_2Cl \xrightarrow[\text{heat}]{H_2SO_4} \ldots \xrightarrow[200\text{-}240^\circ C]{\text{fusion with KOH}} \ldots$$

558. Give reactions that underlie the commercial method of preparing ethylene oxide.

559. Obtain ethylene oxide from ethylene chlorohydrin; tetrahydrofuran from 4-chloro-1-butanol.

560. Obtain propylene oxide using the Prilezhaev reaction.

561. Suggest a method for preparing monomethyl and dimethyl ethers of ethylene glycol.

B. Properties

562. Draw an atomic-orbital model of a molecule of dimethyl ether. Characterize the C—H and C—O bonds in this compound and also reactivity of the ether.

563. Explain why despite the higher molecular mass, ethers boil at lower temperatures than the corresponding alcohols.

564. Consider the I-R spectrum of ethyl ether (liquid film, Fig. 9). Determine the absorption bands characterizing separate groups of atoms.

565. Give general description of the NMR spectra of the following ethers: (a) $CH_3—O—CH_3$, (b) $CH_3CH_2—O—CH_2CH_3$. Indicate the values of chemical shifts expected for the available protons and character of the spin-spin interaction.

566*. What compounds are formed by the following reactions?

(a) $CH_3—O—CH_3+HCl\,(gas) \rightleftharpoons \ldots$

(b) $C_2H_5—O—C_2H_5+BF_3 \rightleftharpoons \ldots$

(c) $CH_3—O—CH_3+BF_3+HF \rightleftharpoons \ldots$

567. Write the reaction of cleavage of ethyl ether with hydriodic acid. Consider the mechanism of the reaction. Indicate the practical importance of the reaction for the analysis of organic compounds.

568*. What compounds are formed by cleaving (with one mole of hydriodic acid) the following ethers: (a) $CH_3—O—CH_2—CH_3$, (b) $CH_3—O—C(CH_3)_3$? Write balanced equations for the reactions. Consider their mechanisms and give explanations.

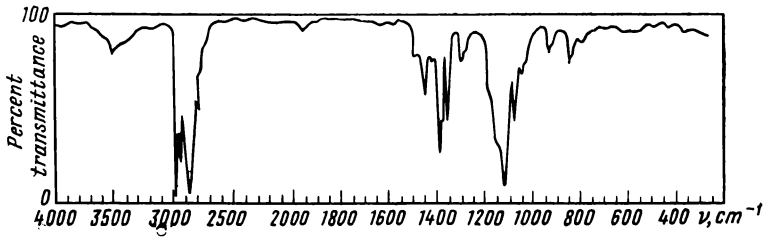


Fig. 9. I-R spectrum of ethyl ether

569. Why is the C—O bond in the type $RCH_2—O—CH_2R$ ethers easier broken by HI than by HBr?

570*. In which solvent, ethyl ether or *n*-hexane, will the reaction of HBr addition to olefin occur faster?

571. Compare the mechanisms of the following reactions:

(a) $C_2H_5—Br+NaOH \longrightarrow C_2H_5OH+NaBr$

(b) $C_2H_5OH+HBr \longrightarrow C_2H_5—Br+H_2O$

(c) $C_2H_5—O—C_2H_5+HBr \longrightarrow C_2H_5Br+C_2H_5OH$

572. Write the reaction of cleaving ethyl ether with: (a) sodium, (b) ethylsodium. Consider the reaction mechanism.

573. Write a balanced equation of the reaction of autooxidation of ethyl ether. What are the properties of the oxidation products?

574. How can the presence of peroxides in ether be established qualitatively? Suggest a method of purification of ethyl ether from peroxides.

575. Compare the character of interaction of ethyl ether and ethyl alcohol with the following substances: (a) sodium

metal, at room temperature, (b) hydrogen chloride, (c) methylmagnesium bromide, (d) concentrated sulphuric acid, at room temperature. Write reaction equations.

576*. Suggest a method for chemical purification of ethyl bromide from ethyl ether admixtures.

577. Compare the properties of ethyl ether and ethyl vinyl ether. Compare their attitude toward the action of dilute acids.

578*. By what spectral method can the following substances be distinguished?

(a) $CH_3CH_2CH_2CH_2OH$ and $CH_3CH_2-O-CH_2CH_3$

(b) $CH_3CH_2-O-CH_2CH_3$ and $CH_3CH_2-O-CH=CH_2$

(c) $CH_3CH_2-O-CH=CH_2$ and $CH_3-O-\underset{\displaystyle CH_3}{\overset{\displaystyle |}{C}}=CH_2$

579. Compare the structure and properties of ethylene oxide and ethyl ether. What accounts for the different reactivity of these compounds?

580. Write a balanced equation for the reaction of ethylene oxide with water in the presence of a mineral acid. Consider the reaction mechanism.

581. How will ethylene oxide react with the following reagents: (a) H—Cl, (b) H—C≡N, (c) C_2H_5OH, (d) NH_3? Write the reactions. Which of the obtained compounds have practical uses?

582. Consider the mechanism of the following reactions:

(a) $\underset{\diagdown\,O\,\diagup}{CH_2-CH_2}+HCl \longrightarrow (OH)CH_2-CH_2Cl$

(b) $CH_3CH_2-O-CH_2CH_3+HBr \longrightarrow CH_3CH_2Br+CH_3CH_2OH$

583. Write polymerization of ethylene oxide. What is the industrial importance of the polymerization product?

THIOALCOHOLS. THIOETHERS

584. Write structural formulas of all compounds having the formula $C_4H_{10}S$. Name them.

585. Name the following compounds:

(a) CH_3SH, (b) $CH_3-CH(CH_3)-CH_2SH$, (c) $C_2H_5-S-C_2H_5$
(d) C_2H_5SK, (e) $CH_3-CH(CH_3)-S-CH(CH_3)-CH_3$

586. Write structural formulas of: (a) ethyl mercaptan, (b) butane-2-thiol, (c) dimethyl sulphide, (d) β,β′-dichlorodiethyl sulphide.

587. Obtain butyl mercaptans from: (a) butyl bromide, (b) butyl alcohol. What is the mechanism of the reaction (a)?

588. Write reactions for preparing diethyl sulphide and methyl ethyl sulphide.

589*. Why does methyl mercaptan (b.p. +6°C) boil at lower temperature than methyl alcohol (b.p. +65°C) and dimethyl sulphide (b.p. +36°C)?

590. Compare the acid properties of alcohols and mercaptans. Explain the differences.

591. Arrange the following compounds in the order of their increasing acid properties: (a) propanol, (b) methylacetylene, (c) propyl mercaptan.

592. Write balanced equations for the reactions of oxidation of methyl mercaptan with: (a) air oxygen, (b) nitric acid. Name the products.

593. Using propyl alcohol and propyl mercaptan, compare the following properties of alcohols and thioalcohols: (a) ability of association, (b) solubility in water, (c) attitude to aqueous solution of alkali, (d) attitude to oxidizing agents.

594. By what reactions can diethyl sulphide be distinguished from its isomer butyl mercaptan?

C. Establishing the Structure of Organic Compounds by Their Properties

595. Write a structural formula of the compound C_4H_8O that fails to liberate methane on treatment with methylmagnesium bromide; when heated with excess HI it forms a mixture of isopropyl iodide and methyl iodide.

596. Determine the structure of the substance $C_5H_{12}O$, the I-R spectrum of which has no absorption in the region of 3600-3000 cm^{-1}. When heated with excess hydrobromic acid, the substance gives a mixture of CH_3Br and C_4H_9Br. The latter compound is dehydrobrominated to give 2-butene.

597. Determine the structure of the substance $C_6H_{14}O$ possessing the following properties: (1) when heated with excess HI it gives isopropyl iodide, (2) it dissolves in con-

centrated sulphuric acid, but is again isolated after dilution with water.

598. Suggest possible structural formulas for the compound $H_{10}S$ characterized by the following properties: (1) it reacts with sodium hydroxide, (2) forms $C_8H_{18}S_2$ on oxidation by atmospheric oxygen.

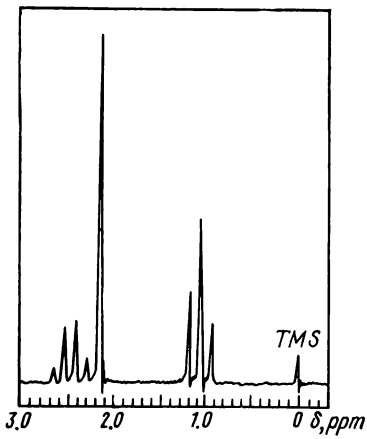


Fig. 10. NMR spectrum of C_3H_8S

599. Write all possible structural formulas for the compound $C_4H_{10}S$, knowing that: (1) it does not react with NaOH, (2) on energetic oxidation it forms $C_4H_{10}SO_2$, (3) when heated with CH_3I it gives $C_5H_{13}SI$.

600*. Establish the structure of the compound C_3H_8S from its NMR spectrum (Fig. 10).

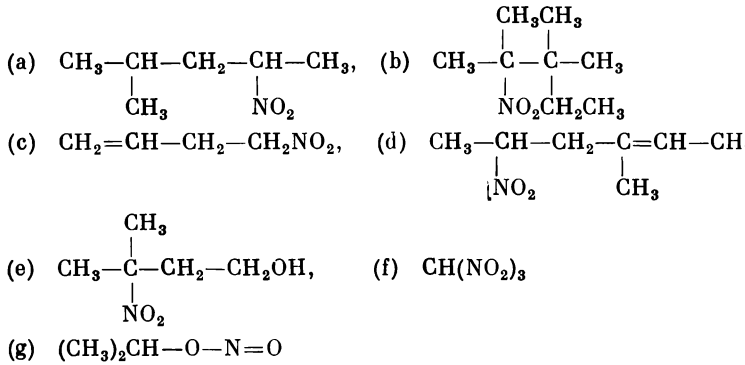
CHAPTER NINE

NITRO COMPOUNDS

A. Isomerism. Nomenclature

601. Write structural formulas of the following compounds: (a) nitroethane, (b) 2-nitro-3-methylbutane, (c) 2-nitro-4,4-dimethylpentane, (d) 4-nitro-2-pentene. Indicate primary, secondary and tertiary nitro compounds.

602. Name the following compounds:



(a) $CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_2-\underset{\displaystyle NO_2}{\underset{|}{CH}}-CH_3$, (b) $CH_3-\overset{\displaystyle CH_3}{\overset{|}{C}}(\overset{\displaystyle CH_3}{\overset{|}{}})-\underset{\displaystyle NO_2}{\underset{|}{C}}(\underset{\displaystyle CH_2CH_3}{\underset{|}{}})-CH_3$

(c) $CH_2=CH-CH_2-CH_2NO_2$, (d) $CH_3-\underset{\displaystyle NO_2}{\underset{|}{CH}}-CH_2-\underset{\displaystyle CH_3}{\underset{|}{C}}=CH-CH_3$

(e) $CH_3-\underset{\displaystyle NO_2}{\underset{|}{\overset{\displaystyle CH_3}{\overset{|}{C}}}}-CH_2-CH_2OH$, (f) $CH(NO_2)_3$

(g) $(CH_3)_2CH-O-N=O$

603. Write structural formulas for all isomers of a compound having the composition $C_4H_9NO_2$. Name them.

604. Write structural formulas of all nitro compounds that are isomers of amyl nitrate. Name them according to the IUPAC system.

B. Methods of Preparing

605. Write the reaction of heating isobutane according to Konovalov. Consider the mechanism of the reaction.

606. What products are formed by nitration of propane in the gaseous phase?

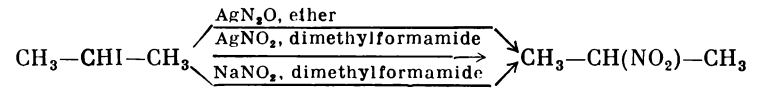
607*. What compounds are formed by the reaction between 1-bromobutane and silver nitrite in ether? Write the reactions and consider their mechanisms. What product is formed in a greater quantity and why?

608*. Explain why 1-iodopropane reacts with silver nitrite in ether to give predominantly the corresponding

nitro compound, while 2-iodopropane gives, in the same conditions, isopropyl nitrite?

609*. Write the reaction of propyl bromide with sodium nitrite in dimethylformamide. Consider its mechanism. What is the role of the solvent? Can this method be used to prepare tertiary nitro compounds?

610*. Analyze the following variants of preparing 2-nitropropane from 2-iodopropane:



In which case will the yield of the nitro compound be the highest and why?

611*. Explain the results of the following conversions:

(a) $CH_3CH_2BrCHCH_3 \xrightarrow[\text{dimethylformamide}]{NaNO_2} CH_3CH_2CH(NO_2)CH_3 + NaBr$

(b) $(CH_3)_3CBr \xrightarrow[\text{dimethylformamide}]{NaNO_2} CH_2{=}C(CH_3){-}CH_3 + NaBr + HNO_2$

612. Accomplish the following transformations:

(a) $ClCH_2{-}COOH \longrightarrow CH_3NO_2$

(b) $CH_3{-}CH(CH_3){-}CH_3 \longrightarrow CH_3{-}\overset{\displaystyle CH_3}{\overset{|}{C}}(NO_2){-}CH_3$

(c) $CH_3{-}CH_2{-}CH{=}CH_2 \longrightarrow CH_3{-}CH_2{-}CH(NO_2){-}CH_3$

(d) $CH_3{-}CH_2{-}CH{=}CH_2 \longrightarrow CH_3{-}CH_2{-}CH(CH_3){-}O{-}N{=}O$

(e) $HC{\equiv}CH \longrightarrow CH_3{-}CH(NO_2){-}CH_3$

(f) $CH_3{-}CH(CH_3){-}CH_2{-}CH_2OH \longrightarrow CH_3{-}CH(CH_3){-}CH_2{-}CH_2NO_2$

C. Structure. Properties

613. Draw the structure of the electron shell of a nitrogen atom. Explain the ability of nitrogen to form compounds with three and also four covalent bonds. Give examples.

614. Discuss the structure of the nitro group. What bond is known as semipolar? What physical methods prove the equivalence of two nitrogen-oxygen bonds in the nitro group?

615. Draw the atomic-orbital model of a molecule of nitromethane. Characterize the C—H bonds in this compound.

616. Consider the effect of the nitro group on the distribution of electron density in a molecule of 1-nitropropane. Characterize the inductive effect of the nitro group.

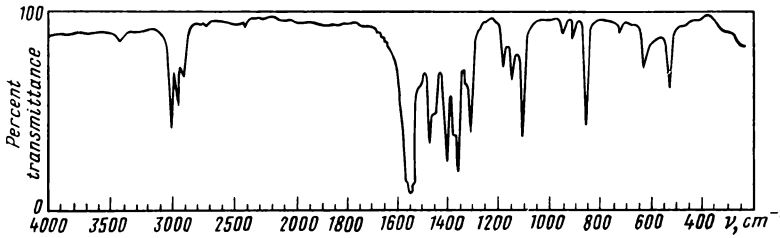


Fig. 11. I-R spectrum of 2-nitropropane

617. Characterize the absorption of nitroalkanes in the U-V region of the electromagnetic spectrum.

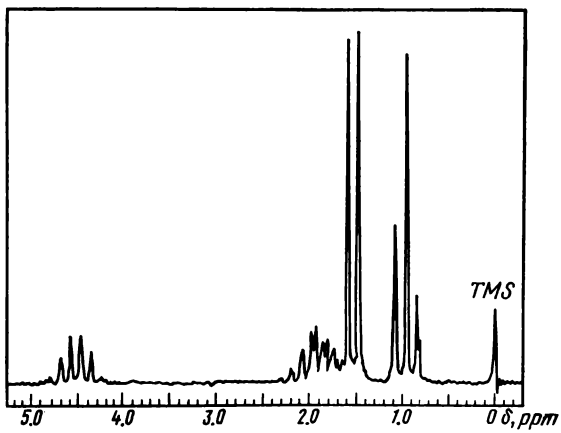


Fig. 12. NMR spectrum of 2-nitrobutane

618. Consider the I-R spectrum of 2-nitropropane (liquid film, Fig. 11). To what region of the spectrum do nitro group frequencies correspond?

619. Figure 12 shows the NMR spectrum of 2-nitrobutane. Interpret the signals.

620. What accounts for the high temperatures at which nitro compounds boil?

621. Obtain ethylamine, isopropylamine from the corresponding nitro compounds.

622. What reactions can be used to distinguish between the following isomers?

(a) $CH_3CH_2CH_2NO_2$ and $CH_3CH_2CH_2O{-}N{=}O$

(b) $CH_3CH_2CH(NO_2)CH_3$ and $CH_3CH_2CH_2CH_2O{-}N{=}O$

623. Using 2-nitropropane as an example, illustrate reactions depending on the presence of an active hydrogen atom in nitro compounds. Indicate the cause of this activity.

624. Compare the attitude of aqueous solutions of alkalis to the following compounds: (a) nitroethane, (b) 2-nitropropane, (c) 3-nitro-3-methylpentane. Consider the mechanism of the reaction. What anion is known as mesomeric?

625. What tautomeric forms are possible for 2-nitrobutane? Write limiting structures of their general mesomeric anion. Compare 'tautomerism' and 'mesomerism'.

626. Indicate which of the following compounds are pseudo-acids: (a) 2-nitrobutane, (b) 2-nitro-2-methylbutane, (c) 1-nitropentane. Prove your answer by the corresponding reactions.

627*. Complete the following:

$$CH_3CH_2CH_2Br \xrightarrow[\text{dimethylformamide}]{NaNO_2} \ldots \xrightarrow{NaOH} \ldots \xrightarrow{Br_2} \ldots$$

$$\ldots \xrightarrow{(CH_3)_2Zn} \ldots$$

628. Compare the attitude of nitrous acid to: (a) 1-nitrobutane, (b) 2-nitrobutane, (c) 2-nitro-2-methylpropane. What is the importance of this reaction for the study of the structure of nitro compounds?

629. By what reactions can nitrobutane isomers be distinguished?

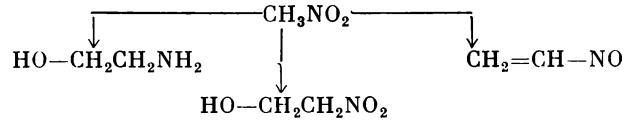
630. Write balanced equations for reactions of nitroethane, and 2-nitrobutane, with formaldehyde in the presence of alkali. What compounds are formed by dehydration of the reaction products? Will 2-nitro-2-methylpropane react with aldehydes?

631*. What compounds are formed by the following reactions?

(a) $CH_3CH(NO_2)CH_3 + HCHO \xrightarrow{(OH^-)} \ldots$

(b) $CH_3NO_2 + 3HCHO \xrightarrow{(OH^-)} \ldots$

632. Accomplish the following transformations:



633*. Complete the following:

(a) $CH_3CH(NO_2)CH_3 + CH_3CH_2CHO \xrightarrow{(OH^-)} \ldots \xrightarrow[\text{heat}]{-H_2O} \ldots$

(b) $CH_3CH_2CH_2OH + HBr \longrightarrow \ldots \xrightarrow[\text{ether}]{AgNO_2} \ldots \xrightarrow[\text{water}]{NaOH} \ldots \xrightarrow{Br_2} \ldots$

(c) $CH_3CH{=}CH_2 + HBr \longrightarrow \ldots \xrightarrow[\text{dimethylformamide}]{NaNO_2} \ldots \xrightarrow{HNO_2} \ldots$

634. Using the Konovalov-Nef reaction, obtain the following compounds from the corresponding nitro compounds: (a) propionic aldehyde, (b) methyl ethyl ketone.

635*. Obtain valeric acid from 1-nitropentane.

D. Establishing the Structure of Organic Compounds by Their Properties

636. Write a structural formula of a compound having the composition $C_5H_{11}NO_2$ that does not react with an aqueous solution of alkali.

637. What is the structure of a tertiary nitro compound having the composition $C_8H_{17}NO_2$ if its basic hydrocarbon can be obtained from a primary alkyl halide by the Wurtz reaction as the only reaction product.

638*. Write a structural formula of the compound $C_4H_8NO_2Na$ that forms methyl ethyl ketone with excess mineral acid.

639*. The compound $C_4H_9NO_2$ reacts with acetaldehyde to give $C_6H_{13}NO_3$ which is dehydrated to give 3-nitro-4-methyl-2-pentene. Write a structural formula of the original compound.

640*. Establish the structure of the compound $C_3H_7NO_2$ by its I-R (liquid film) and NMR spectra (Figs. 13 and 14).

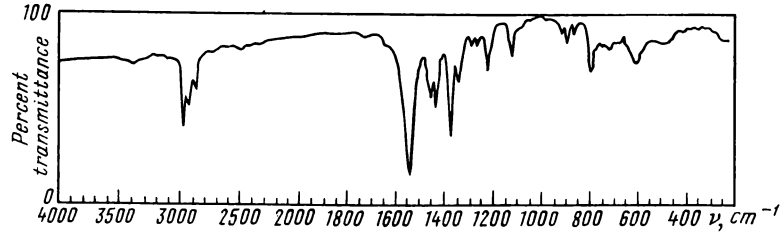


Fig. 13. I-R spectrum of $C_3H_7NO_2$

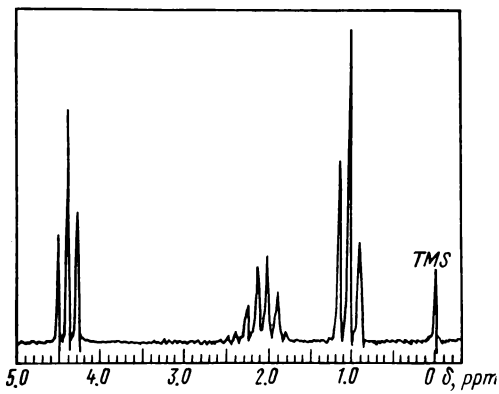


Fig. 14. NMR spectrum of $C_3H_7NO_2$

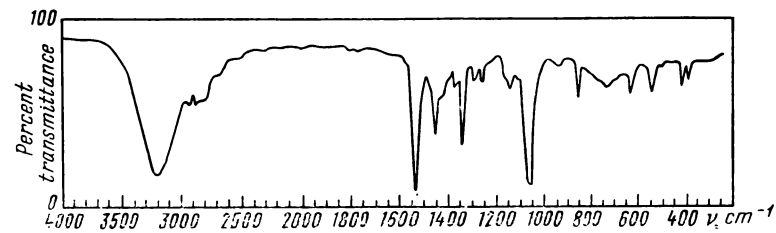


Fig. 15. I-R spectrum of $C_4H_9NO_5$

641*. Heating nitromethane with formaldehyde in the presence of alkali gives the compound $C_4H_9NO_5$. Its I-R spectrum (on KBr plate) is given in Fig. 15. What conclusion concerning the structure of the obtained compound can be made?

CHAPTER TEN

AMINES

A. Isomerism. Nomenclature

642. Name the following amines:

(a) $CH_3CH_2CH_2—NH_2$, (b) $(CH_3)_2CH—NH_2$, (c) $H_2N—CH_2CH_2—NH_2$
(d) $CH_3—NH—C_2H_5$, (e) $(CH_3)_2N—CH_2CH_2CH_2CH_3$, (f) $(CH_3)_3C—NH_2$

Indicate primary, secondary and tertiary amines.

643. Write structural formulas of the following compounds: (a) *sec*-butylamine, (b) di-*tert*-butylamine, (c) methylethylisopropylamine, (d) 1,3-pentanediamine, (e) dimethylbutylamine.

644. Write structural formulas for all isomers of the compounds having the compositions C_3H_9N and $C_4H_{11}N$. Name them.

645. Name the following compounds:

(a) $CH_3CH_2CH(CH_3)NH_2$, (b) $(CH_3CH_2)_3N \cdot HCl$
(c) $(CH_3CH_2)_2NCH(CH_3)_2$, (d) CH_3CONH_2
(e) $[(CH_3CH_2)_4N]^+Br^-$, (f) $CH_3CONHCH_3$

B. Methods of Preparing

646. What compounds are formed by the reaction of ethyl iodide with ammonia? Consider the mechanism of the reaction of N-alkylation.

647. By the action of what reagents can free amines be isolated from (a) trimethylammonium chloride, (b) methylpropylammonium iodide? Write the reactions.

648. What compounds are obtained by heating ethyl alcohol with ammonia in the presence of Al_2O_3? Write the reactions.

649. Obtain isopropylammonium bromide from propylene and inorganic reagents.

650. Accomplish the following transformations:

$$CH_2=CH_2 \rightarrow \begin{cases} CH_3CH_2NHCH_3 \\ CH_3CH_2CH_2NH_2 \\ [CH_3CH_2N(CH_3)_3]^+I^- \end{cases}$$

651. Obtain propylamine by the Gabriel phthalimide reaction. Indicate the advantage of this method over alkylation of ammonia with alkyl halides and alcohols.

652*. Obtain propylamine uncontaminated by secondary and tertiary amines using propyl iodide.

653. Obtain propylamine from propionic aldehyde by reductive alkylation of ammonia. What compound can be used to prepare methylpropylamine by the same method?

654. What amines can be produced by reducing the following compounds: (a) 1-nitropropane, (b) 2-nitrobutane? Specify the reaction conditions.

655. What amines can be obtained by reduction of the following compounds: (a) aldoxime, (b) propionitrile, (c) methylcarbylamine, (d) 2-nitro-2-methylpropane, (e) adipic dinitrile. Specify the reaction conditions.

656. What compounds are formed by reduction of (a) butyramide, (b) propionitrile, with $LiAlH_4$?

657. Use propionamide to prepare ethylamine by the Hofmann rearrangement.

658*. Which is a better method of preparing *tert*-butylamine: (a) by alkylation of ammonia, or (b) from an acid amide by the Hofmann rearrangement? Develop your reasons.

659. Obtain amylamine and butylamine from valeric acid.

660. Obtain butylamine (a) by the alkylation of ammonia, (b) by the phthalimide method, (c) by the Hofmann rearrangement.

661. Obtain hexamethylenediamine from adipic acid.

C. Structure and Properties

662. Consider the electronic and spatial structure of a methylamine molecule.

663*. Explain why tertiary amines having various hydrocarbon radicals attached to nitrogen atom do not show optical activity.

664. Explain why methylamine boils at temperatures much higher (—6.5°C) than methane (—161.7°C), but lower than methyl alcohol (+64.7°C).

665. Characterize the spectral properties of amines. What information concerning their structure can be obtained from the I-R and NMR spectra?

666*. The alpha-carbon bonded hydrogen atom of nitro compounds is very active, whereas the amine hydrogen (in a similar position to the amino group) is not. Explain.

667. What accounts for the main properties of amines? What is the base constant of amines (K_b)? Arrange the following compounds in the order of their increasing basicity in an aqueous solution: methylamine, dimethylamine, trimethylamine.

668. Which of the following compounds has the strongest basic properties: (a) $(CH_3CH_2)_2NH$, (b) $[(C_2H_5)_4N]^+OH^-$, (c) $CH_3CH_2—NH_2$? Which of them is the weakest base? Develop your reasons.

669*. What spectral method can be used to distinguish between the following three compounds: (a) hexylamine, (b) ethylbutylamine, (c) triethylamine?

670. Name the following compounds:

(a) $[CH_3NH_3]^+Cl^-$, (b) $[(CH_3)_2CHNH_2(CH_3)]^+HSO_4^-$

(c) $[(CH_3)_3CNH_3]^+Br^-$

Write balanced equations of the reactions for their preparation. How can free bases be isolated from these salts?

671. Obtain diethylamine and triethylamine from ethylamine. Consider the mechanism of N-alkylation with halogen derivatives. What chemical method should be used to separate the mixture of the original amine and the reaction products?

672. Obtain tetrapropylammonium iodide from propyl bromide. Draw a spatial structure of tetrapropylammonium cation. How can a free quaternary ammonium base be obtained from the ammonium salt?

673. Write reactions for preparing: (a) tetraethylammonium bromide, (b) dimethyloxonium chloride, (c) triethylsulphonium iodide. On what specific feature of the electronic structure of amines, ethers, and thioethers does their ability to give onium compounds depend?

674. Write the reaction occurring on heating of tetramethylammonium hydroxide. Consider the reaction mechanism.

675. What compounds can be obtained by heating (a) trimethylethylammonium hydroxide, (b) dimethylethylpropylammonium? Formulate the Hofmann rule.

676*. What are the products of thermal decomposition of the following hydroxides:

(a) $[CH_3CH_2CH_2CH_2—N(CH_3)_2—CH_2CH_3]^+OH^-$

(b) $[ClCH_2CH_2—N(CH_3)_2—CH_2CH_3]^+OH^-$

677. How can propylamine be acetylated? Write the reaction. Compare the basic properties of the original and the end products.

678. Compare the attitude of propylamine, methylethylamine, and trimethylamine to nitrous acid. Consider the reaction mechanism using propylamine as an example. What is the importance of the reaction of amines with nitrous acid?

679. What principle underlies the method of separation of primary, secondary, and tertiary amines using benzene sulphochloride?

680. What is the product of the reaction of methylamine, chloroform, and an alkali with heating? Indicate the importance of this reaction.

681*. What compound is formed by oxidizing triethylamine with hydrogen peroxide or percarboxylic acids? Consider the character of bonds in the obtained product and its spatial structure.

682. Write the reaction of propylamine with HCl, acetic anhydride, ethyl iodide, and nitrous acid. Consider the reaction mechanisms.

683. Which of the following amines: (a) ethylamine, (b) methylpropylamine, (c) triethylamine, will react with: (a) HCl, (b) CH_3I, (c) CH_3COCl, (d) HNO_2? Write the reactions.

684. Write structural formulas of the following compounds: (a) an amine, having the composition $C_4H_{11}N$, that does not enter the acylation reaction, (b) an amide that undergoes the Hofmann rearrangement to give isobutylamine.

D. Establishing the Structure of Organic Compounds by Their Properties

685. What is the structure of an amine having the composition $C_4H_{11}N$? It does not react with acetic anhydride and reacts with only one molecule of methyl iodide.

686. Write a structural formula of an amine formed from isovaleramide, $(CH_3)_2CHCH_2CONH_2$, by the Hofmann rearrangement.

687. Establish the structure of a compound having the composition $C_4H_{11}N$ that: (a) reacts with HNO_2 to give $C_4H_{10}N_2O$, (b) when acted upon with excess CH_3I, and then with AgOH, and finally heated, it forms trimethylamine, propylene, and water.

688*. Establish the structure of an amine having the composition $C_4H_{11}N$ from the following: (a) the I-R spectrum has one absorption band in the region of 3500-3300 cm^{-1} (about 3330 cm^{-1}); (b) the NMR spectrum has three signals (with respect to tetramethylsilane): δ_1 0.8 ppm (singlet), δ_2 1.1 ppm (triplet) and δ_3 2.7 ppm (quartet).

689*. A compound having the composition $C_6H_{15}N$ has the following properties: (1) when acted upon with HNO_2 it gives $C_6H_{14}N_2O$; (2) when treated with excess CH_3I, then with AgOH, and finally heated, it gives 3-methyl-1-butene. Write the structural formula of the compound $C_6H_{15}N$.

690*. The compound $C_5H_{11}NO_2$ is reduced into the compound $C_5H_{13}N$ that is soluble in acids. When $C_5H_{13}N$ is acted upon by excess CH_3I, with subsequent treatment with AgOH, it gives $C_8H_{21}NO$. The latter is decomposed on heating to give trimethylamine and 2-methyl-1-butene. Establish the structure of the original compound $C_5H_{11}NO_2$.

691*. Establish the structure of the amine $C_6H_{15}N$ by the following: (1) it does not absorb in the I-R spectrum in the region of 3500-3200 cm^{-1}, (b) the NMR spectrum has two singlets: δ_1 1.00 ppm and δ_2 2.10 ppm, their intensities relating 3 : 2.

CHAPTER ELEVEN

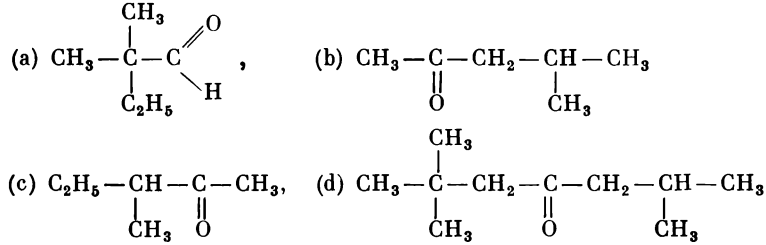
ALDEHYDES AND KETONES

A. Isomerism. Nomenclature

692. Write structural formulas for all isomers of aldehydes and ketones having the formula C_4H_8O. Give their IUPAC names.

693. Write structural formulas of the following compounds: (a) propionaldehyde, (b) isovaleraldehyde, (c) diisopropyl ketone, (d) trimethylacetaldehyde, (e) 3-methylpentanal, (f) 2-hexanone.

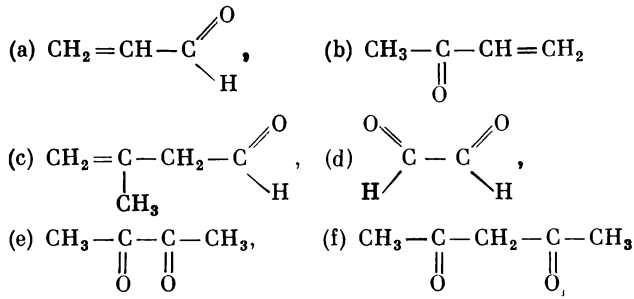
694. Name the following carbonyl compounds:



695. Draw structural formulas of all isomers of methyl ketone having the composition $C_6H_{12}O$. Name them.

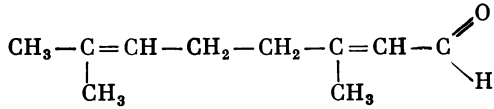
696. Write formulas of ketones that are isomers to capraldehyde. Name them.

697. Name the following carbonyl compounds:



698. Write structural formulas of the following compounds: crotonaldehyde, methyl allyl ketone, 2,3-pentanedione, 4-methyl-2-pentenal, 2-methyl-2-butenal, ketene.

699*. How many stereoisomers have the following structure?



In what do they differ? Name them.

700. Write structural formulas of (a) the simplest dialdehyde, (b) the simplest alpha-, beta-, and gamma-diketones. Name them.

B. Methods of Preparing

701. Prepare propionaldehyde: (a) from olefins by oxo synthesis, ozonolysis, (b) by hydrolysis of dihalogen derivatives, (c) by oxidation of a monohydric alcohol, (d) by thermal decomposition of a mixture of carboxylic acids, (e) by reduction of carboxylic acid chloride, (f) by the Grignard reaction.

702. Write the reaction of preparing methyl ethyl ketone: (a) by dehydrogenation of an alcohol, (b) by ozonolysis of an olefin, (c) by dry distillation of Ca salts of carboxylic acids, (d) by the Grignard method, (e) by the Kucherov method.

703. What aldehydes are obtained by oxo synthesis from 1-butene, 2-butene? Write the reactions.

704. What compounds are formed by hydration of the following hydrocarbons by the Kucherov reaction: (a) acetylene, (b) methylacetylene, (c) butylacetylene?

705. Complete the following:

$$H-C\equiv C-H+C_2H_5OH \xrightarrow[KOH]{} \ldots \xrightarrow[(H^+)]{H_2O} \ldots$$

What is the advantage of the commercial method of the manufacture of acetaldehyde from acetylene through vinylalkyl ethers over the Kucherov method?

706. Accomplish the following transformations:

(a) $CH_3-CH_2-CHCl_2 \longrightarrow CH_3-CH_2-CHO$

(b) $CH_3-CCl_2-CH_2-CH_3 \longrightarrow CH_3-CO-CH_2CH_3$

707. What carbonyl compounds are formed by oxidation of the following alcohols:

(a) $CH_3CH_2CH_2OH$, (b) $CH_3-CH(CH_3)-CH(OH)-CH_2CH_3$

(c) $HO-CH_2-CH(CH_3)_2$, (d) $(OH)CH_2-CH_2-CH_2-CH_2(OH)$

Name the starting and end products.

708. By oxidation of what alcohols can the following aldehydes and ketones be obtained: (a) methyl ethyl ketone, (b) isopropylacetaldehyde, (c) trimethylacetaldehyde, (d) ethyl-*sec*-butylketone?

Write the reactions and specify their conditions.

709. What compounds are formed by catalytic dehydrogenation of: (a) methyl alcohol, (b) *sec*-propyl alcohol, (c) *sec*-isoamyl alcohol?

710*. What products are formed by the oxidation of the following α-glycols with periodic acid?

(a) $CH_3-CH(OH)-CH(OH)-CH_3$

(b) $CH_2(OH)-\underset{\displaystyle CH_3}{\overset{\displaystyle |}{C}}(OH)-CH_2-CH_3$

What is the importance of the oxidation reaction of alpha-glycols with periodic acid?

711*. Complete the following:

$$CH_3-\underset{\displaystyle CH_3}{\overset{\displaystyle |}{C}}=CH-CH_3-\begin{cases}\xrightarrow{O_3}\ \ldots\ \xrightarrow{+H_2O}\ \ldots\\ \xrightarrow[(H_2O),\ 20^\circ C]{KMnO_4}\ \ldots\ \xrightarrow{+HIO_4}\ \ldots\end{cases}$$

712*. How can the following conversion be accomplished?

$$(CH_3)_2CH-CH_2CH_2OH \longrightarrow (CH_3)_2CH-CHO$$

713. Using butyl alcohol obtain: (a) butyric aldehyde, (b) methyl ethyl ketone.

714. Write the reaction that occurs as acetic acid vapour is passed over a heated catalyst (ThO_2, MnO_2). What product will be obtained if a mixture of acetic and propionic acids, or else of propionic and formic acids, is taken?

715. Obtain methyl propyl ketone, diisopropyl ketone and valeraldehyde by pyrolysis of calcium salts of the corresponding carboxylic acids.

716. Using butyl alcohol obtain: (a) dipropyl ketone, (b) dibutyl ketone. Write the reactions.

717. Write the synthesis of diisopropyl ketone (a) by oxidation of the corresponding alcohol, (b) by dry distillation of calcium salts of a carboxylic acid, (c) by ozonolysis of the corresponding ethylene hydrocarbon. Can this ketone be obtained by hydration of an acetylene hydrocarbon in the Kucherov reaction?

718. Write the reaction of ethylmagnesium bromide with the following compounds: (a) triethyl orthoformate, (b) acetonitrile. What substances are formed by hydrolysis of the obtained products?

719. Write the synthesis of butyric and isobutyric aldehydes using triethyl orthoformate and the corresponding Grignard reagent.

720. Using a nitrile of the corresponding acid, obtain methyl butyl ketone by the Grignard reaction.

721. Using butyronitrile obtain methyl isopropyl ketone.

722. What compounds are formed: (a) during the pyrolysis of acetone, (b) by the action of zinc dust on bromoanhydride of alpha-bromoisobutyric acid?

723. Synthesize the following compounds: (a) $CH_3—CH=CH—CHO$ from acetaldehyde, (b) $(CH_3)_2C=CH—CO—CH_3$ from acetone.

C. Structure and Properties

724. Give the spectral characteristics of saturated aldehydes and ketones.

725. Characterize the infra-red (liquid film), ultra-violet (heptane), and NMR spectra of methyl ethyl ketone (Figs. 16-18).

726. Characterize the structure of the carbonyl group. What is the similarity and difference between the $\rangle C=O$ and $\rangle C=C\langle$ bonds?

727. What type of reactions is more common for the carbonyl group of aldehydes and ketones? What is the mechanism of these reactions?

728. Arrange the following compounds in the order of their growing affinity for nucleophilic addition reactions: (a) $CH_3—CO—CH_3$, (b) $H—CHO$, (c) $(CH_3)_3C—CO—C(CH_3)_3$, (d) $CH_3CH_2—CHO$. Develop your reasons.

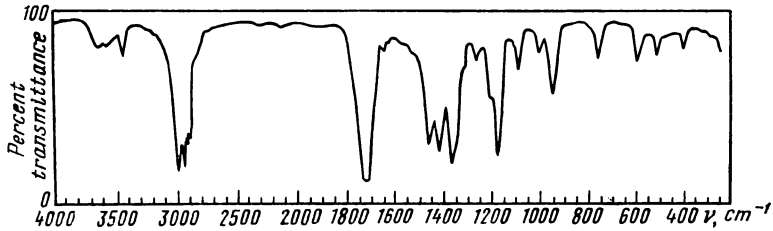


Fig. 16. I-R spectrum of methyl ethyl ketone

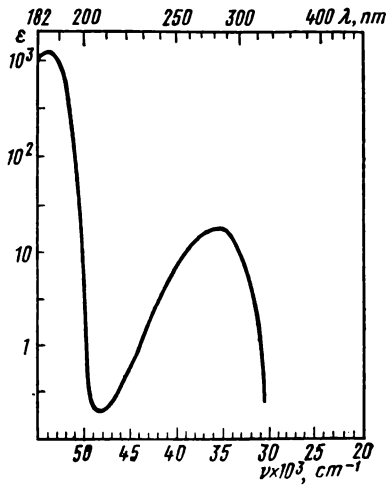


Fig. 17. U-V spectrum of methyl ethyl ketone

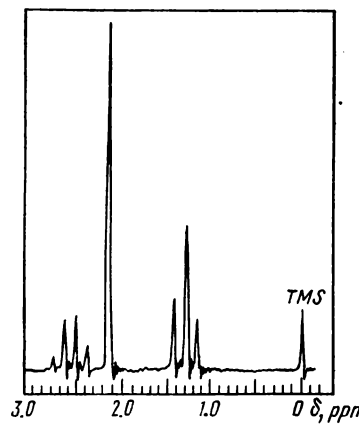


Fig. 18. NMR spectrum of methyl ethyl ketone

729. Which of the compounds given below in pairs is easier to react with nucleophilic reagents?

(a) $CH_3CH_2CH_2—CHO$ or $CH_3—CO—CH_3$

(b) $CH_3CH_2—CO—CH_2CH_3$ or $(CH_3)_2CH—CO—CH(CH_3)_2$

(c) $CH_3—CHO$ or $Cl_3C—CHO$

730. Explain the following facts: (1) the boiling point of an aldehyde (ketone) is lower than that of the corresponding alcohol, (2) lower aldehydes and ketones boil at temperatures 50-80°C higher than the boiling points of hydrocarbons having the same molecular mass.

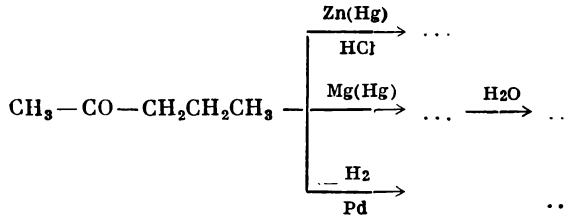
731. Indicate reactions common for butyraldehyde and methyl ethyl ketone. Indicate differences in their chemical properties.

732. What compounds are formed by catalytic reduction of methyl ethyl ketone, isobutyraldehyde, diisopropyl ketone?

733. What products are obtained during reduction, by the Meerwein-Ponndorf-Verley method, of: (a) valeraldehyde, (b) dipropyl ketone? How can the yield of the reaction products be increased?

734*. Write the reduction of butyric and crotonaldehydes: (a) with hydrogen in the presence of Ni, (b) with lithium aluminium hydride. What is the advantage of the latter reducing agent?

735. Complete the following:



736*. Write the reaction of acetone, and also propionaldehyde with HCN. Consider the reaction mechanism. Which of the two compounds will easier react with HCN? Why? Explain why the formation of cyanohydrin is accelerated by adding bases and retarded by acids.

737. Obtain the following hydroxy nitriles:

(a) $CH_3-CH(CH_3)-CH(OH)-CN$

(b) $CH_3CH_2-\underset{\displaystyle CN}{\overset{\displaystyle |}{C}}(OH)-CH_2CH_2-CH(CH_3)-CH_3$

from the corresponding carbonyl compounds.

738. Which of the following aldehydes and ketones will give bisulphite derivatives: (a) acetaldehyde, (b) acetone,

(c) diisopropyl ketone, (d) ethyl propyl ketone, (e) trimethylacetaldehyde? Write a balanced equation of the reaction for one of the above compounds. How can an aldehyde (or a ketone) be isolated from the corresponding bisulphite derivative? Write balanced equations of the reactions.

739*. Using the reaction of acetone with $NaHSO_3$ as an example, consider the mechanism of the formation of a bisulphite derivative. Why does the addition of HCN to aldehydes and ketones require a catalyst, whereas $NaHSO_3$ is added easily and without catalysts?

740. Suggest a chemical method of separation of a mixture of valeraldehyde, valeric acid, and amyl alcohol.

741. Write the reactions of formaldehyde, acetaldehyde, and acetone with propylmagnesium iodide. Consider the mechanism of one of the reactions.

742. Give three examples of nucleophilic addition reaction (across the carbonyl group) that are accompanied by spontaneous dehydration.

743. Write the reaction of acetaldehyde with ammonia. Consider the mechanism.

744. Write the reactions of acetone with hydroxylamine, hydrazine, and phenylhydrazine. Name the products obtained. Illustrate the similarity of the mechanisms of these reactions.

745. Use the Kishner reaction to obtain heptane: (a) from heptanal, (b) from methyl amyl ketone.

746*. Explain why the product of addition of ammonia to acetaldehyde fails to be isolated, whereas chloral ammonia is quite stable and can be isolated and identified.

747. Write the following transformations:

(a) $CH_3CH_2-CHO \longrightarrow CH_3CH_2CHCl_2$

(b) $CH_3CH_2-CO-CH_3 \longrightarrow CH_3-C\equiv C-CH_3$

(c) $CH_3CH_2-CHO \longrightarrow CH_3-CO-CH_3$

748*. Give reactions of acetaldehyde in which the alpha-carbon bonded hydrogen takes part. What accounts for the activity of this atom? Why is the hydrogen of the aldehyde group not active?

749. Which of the following carbonyl compounds: (a) heptanal, (b) trimethylacetaldehyde, (c) isobutyraldehyde,

(d) acetone, (e) formaldehyde, can take part in the aldol condensation reaction? Indicate compounds that can participate in the croton condensation.

750. Write the aldol and croton condensation: (a) of acetaldehyde, (b) propionaldehyde, (c) butyraldehyde.

751. Using propionaldehyde as an example, consider the mechanism of the aldol condensation in conditions of alkaline catalysis.

752*. What reaction products can be expected in the following aldol condensation reactions?

(a) $H-CHO+CH_3COCH_3 \xrightarrow{NaOH} \ldots$

(b) $H-CHO+(CH_3)_2CH-CHO \xrightarrow{NaOH} \ldots$

753*. Accomplish the following conversion:

$$(CH_3)_2CHCH_2CH_2OH \longrightarrow (CH_3)_2CH-CH_2CH=\underset{\displaystyle CH(CH_3)_2}{\overset{\displaystyle |}{C}}-CHO$$

754*. Using the aldol condensation, synthesize the following: (a) 4-hydroxy-2-pentanone, (b) 3-methyl-4-hydroxy-2-pentanone, (c) 4-hydroxy-2-heptanone.

755. What compounds are formed in the reaction between propionaldehyde and: (a) CH_3NO_2, (b) $CH_3-CH(NO_2)-CH_3$ in the presence of a base?

756*. Write the reaction between acetone and bromine (1 : 1). Compare the mechanisms of the reaction of bromination of acetone and methane.

757*. Knowing the mechanism of the halogenation of carbonyl compounds, explain the following: (a) the rate of bromination of acetone does not depend on the concentration of bromine, (b) acetone reacts with all halogens at an equal rate.

758*. Which of the following ketones gives the haloform reaction: (a) diethyl ketone, (b) acetone, (c) methyl propyl ketone, (d) diisopropyl ketone? Write the reaction equations.

759. Suggest chemical reactions to distinguish between butyraldehyde and methyl ethyl ketone. Can these compounds be differentiated by their I-R spectra?

760. What products are formed by oxidation of the following carbonyl compounds: (a) formaldehyde, (b) ethyl

isopropyl ketone, (c) butyraldehyde, (d) methyl ethyl ketone, (e) ethyl propyl ketone?

Indicate compounds that are the easiest to be oxidized.

761. Write a balanced equation for the reaction of oxidation of propionaldehyde with silver oxide in an aqueous solution of ammonia (the silver mirror reaction).

762. Consider the mechanism of autooxidation of aldehydes using butanal as an example.

763. Write a structural formula of a ketone, the oxidation of which gives a mixture of acetic, propionic, valeric, and caproic acids.

764. What reaction takes place during dissolution of formaldehyde in water? Consider the mechanism of the process. Can the product of this reaction be isolated? What facts prove the formation of hydrate forms of lower aldehydes in an aqueous solution?

765*. Compare and explain the different stability of hydrate forms of the following carbonyl compounds:

(a) CH_2O and CH_3CHO, (b) CH_3-CHO and Cl_3C-CHO

(c) $CH_3-CO-CH_3$ and $F_3C-CO-CF_3$

(d) $HOOC-CHO$ and $H_5C_2OOC-CHO$.

766. Compare the ability to hydration of the bonds $\diagdown C=O$ and $\diagdown C=C\diagup$ using formaldehyde and ethylene as examples. Compare the mechanisms of the reactions.

767. Obtain hemiacetal and also acetal from acetaldehyde and methyl alcohol.

768. Consider the mechanism of the reactions and explain why an aldehyde hemiacetal can be formed in conditions of acid and basic catalyses, whereas an acetal (from aldehyde and alcohol), only in conditions of acid catalysis.

769*. What acetals are formed in the following reactions (molar ratio of aldehyde to alcohol, 1 : 5):

(a) $CH_3CHO + 2C_2H_5OH \xrightarrow{(H^+)} \ldots$ (78%)

(b) $CH_3CHO + 2(CH_3)_3COH \xrightarrow{(H^+)} \ldots$ (23%)

(c) $(CH_3)_3C-CHO + 2C_2H_5OH \xrightarrow{(H^+)} \ldots$ (56%)

(d) $(CH_3)_3C-CHO + 2(CH_3)_2CHOH \xrightarrow{(H^+)} \ldots$ (11%)

Explain the cause of decreasing yields in transition from reaction (a) to (b) and from (c) to (d).

770. By the action of what reagents can the following transformations be accomplished:

(a) $ClCH_2-CH_2-CHO \longrightarrow ClCH_2-CH_2-CH(OC_2H_5)_2 \longrightarrow$

$\longrightarrow CH_2=CH-CH(OC_2H_5)_2 \longrightarrow CH_2=CH-CHO$

(b) $CH_2=CH-CHO \longrightarrow CH_2Br-CHBr-CHO \longrightarrow$

$\longrightarrow CH_2Br-CHBr-CH(OC_2H_5)_2 \longrightarrow$

$\longrightarrow HC\equiv C-CH(OC_2H_5)_2 \longrightarrow HC\equiv C-CHO$

771*. Chloral Cl_3C-CHO quickly reacts with methanol to give hemiacetal, but only slowly converts into acetal in the presence of acid. Explain.

772. Which of the following aldehydes: (a) acetaldehyde, (b) formaldehyde, (c) isobutyraldehyde, (d) trimethylacetaldehyde, and (e) glyoxal, OHC—CHO, will be active in the Cannizzaro reaction? Write the reactions.

773. What products can be formed by the action of concentrated solution of KOH on a mixture of formaldehyde and trimethylacetaldehyde?

774. Write formulas of polymers of formic and acetic aldehydes. Describe their properties.

775. Figure 19 shows the U-V spectra of methyl ethyl ketone and methyl vinyl ketone (in cyclohexane). Identify the curves. What differences are found in these compounds from their I-R spectra?

776. What products are formed by catalytic hydrogenation of: (a) acrolein, (b) 4-pentenal? What is the attitude of acrolein and 4-pentenal to the action of sodium amalgam in an aqueous-alcoholic solution?

777. Complete the following:

$$CH_2=CH-CHO \begin{cases} \xrightarrow{KMnO_4(H_2O),\ 20^\circ C} \ldots \\ \xrightarrow[NH_4OH]{AgNO_3} \ldots \end{cases}$$

778. Complete the following:

$$2CH_3COCH_3 \xrightarrow[(H_2O,\ heat)]{NaOH} \ldots \xrightarrow{HBr} \ldots$$

779. Give examples of nucleophilic addition reactions

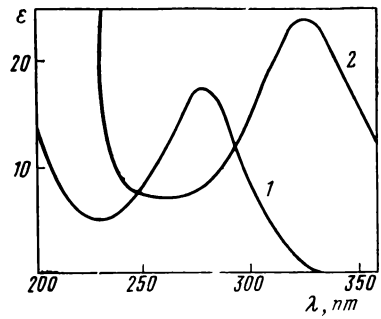


Fig. 19. U-V spectra of methyl ethyl ketone and methyl vinyl ketone

for acrolein: (a) to the $\rangle C=O$ group, (b) to the $\rangle C=C\langle$ bond.

780. Complete the following:

$$CH_2=CH-CHO \xrightarrow{+HCl} \ldots \xrightarrow[H^+]{2C_2H_5OH} \ldots \xrightarrow[alcohol]{+KOH} \ldots$$

$$\ldots \xrightarrow[in\ the\ cold]{KMnO_4} \ldots \xrightarrow[H^+]{+HOH} \ldots$$

781*. Indicate the active hydrogen atom in the following aldehydes: (a) CH_3CHO, (b) $CH_3-CH=CH-CHO$, (c) $CH_3-CH=CH-CH=CH-CHO$. Write the reactions of the aldol and croton condensations of these aldehydes.

782. Characterize the structure of the simplest ketene.

783. Write the reaction of ketene with water, alcohol, and acetic acid. Consider the reaction mechanisms.

784*. What reactions can be used to distinguish between the following isomers:

(a) $CH_2=CH-CH_2-CH_2-CHO$ and $CH_3CH_2CH=CH-CHO$

(b) $CH_2=CH-CHO$ and $CH_3CH=C=O$

(c) $CH_3CH=CH-CO-CH_3$ and $CH_2=CH-CH_2-CO-CH_3$

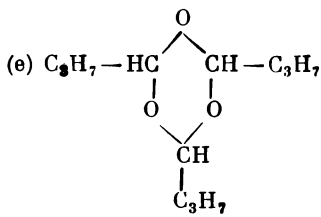
Can they be distinguished by the spectral methods?

785. Give reactions characterizing specific properties of formaldehyde (compared with the properties of its homologues).

786. Name the following substances and give reactions for their preparing from the corresponding carbonyl compounds:

(a) $CH_3-\underset{\displaystyle CN}{\underset{|}{C}}(OH)-CH_2CH_2CH_3$, (b) $CH_3CH_2-CH_2-CH(OH)-SO_3Na$

(c) $F_3C-CH(OH)_2$, (d) $CH_3-\underset{\displaystyle N(OH)}{\underset{\|}{C}}-\underset{\displaystyle N(OH)}{\underset{\|}{C}}-CH_3$

(e) 

(f) $CH_3CH_2-CH(OH)-CH(CH_3)-CHO$

787*. Suggest the method of the following conversion:

$$CH_3-CO-CH_2CH_2-CHO \longrightarrow HOOC-CH_2CH_2-CHO$$

788. Give examples of the following compounds: (a) an aldehyde that does not enter the aldol condensation, (b) an aldehyde giving an aldol but forming no aldehyde of the croton type, (c) a ketone that does not give bisulphite derivatives, (d) a ketone participating in the haloform reaction, (e) a diketone that is oxidized to give only one acid.

D. Establishing the Structure of Organic Compounds by Their Properties

789. Write a structural formula for the compound $C_7H_{14}O$ that: (a) has an intense absorption band at 1715 cm^{-1} in the I-R spectrum, (b) is hydrogenated into $C_7H_{16}O$, the dehydrogenation and subsequent ozonolysis of which give a mixture of propionaldehyde and methyl ethyl ketone.

790. Determine the structure of the substance C_4H_8O the I-R spectrum of which has an intense absorption band

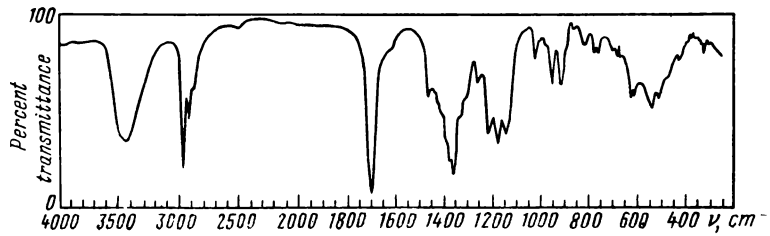


Fig. 20. I-R spectrum of $C_6H_{12}O_2$

at 1720 cm^{-1}. The oxidation of the original compound gives acetic acid as the main reaction product.

791. The substance $C_5H_{12}O$ has the following properties: (a) it is oxidized to give $C_5H_{10}O$ that reacts with phenylhydrazine, (b) its dehydrogenation gives the hydrocarbon C_5H_{10} the oxidation of which gives acetone among other products. What is the structure of the original compound?

792. Determine the structure of a liquid having the formula C_3H_6O, the I-R spectrum of which has a strong absorption band at 1730 cm^{-1}. The substance is easily oxidized to $C_3H_6O_2$.

793*. In the presence of alkaline catalysts, acetone gives in the cold a product having the composition $C_6H_{12}O_2$, the I-R spectrum of which (liquid film) is shown in Fig. 20. What conclusion concerning the structure of this compound can be drawn?

794. A substance having the formula $C_5H_{10}O$ forms an oxime, gives the iodoform reaction with NaOI, and is oxi-

dized into a mixture of acids, one of which is propionic. What is the structure of the substance $C_5H_{10}O$?

795*. What compound is obtained by hydration of vinylacetylene in the Kucherov reaction? Suggest chemical and spectral methods that can be used to prove its structure.

796. The substance $C_5H_8O_4Ca$ undergoes dry distillation to give C_4H_8O that reacts with hydroxylamine but does

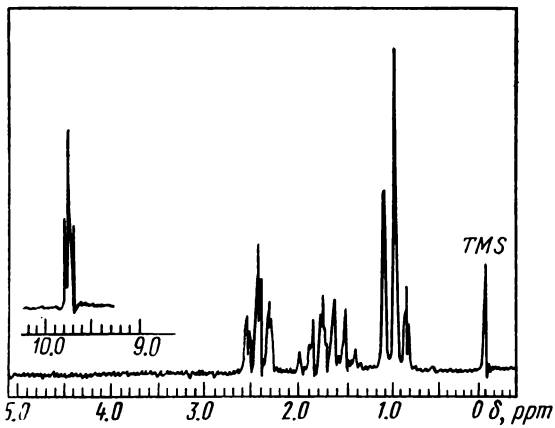


Fig. 21. NMR spectrum of C_4H_8O

not give the silver mirror reaction. Establish the structure of $C_5H_8O_4Ca$ and the obtained compound C_4H_8O.

797. Establish the structure of the compound $C_5H_8O_2$ that gives a dioxime, produces a positive iodoform reaction, reduces ammoniacal silver oxide solution, and is converted into *n*-pentane on complete reduction.

798*. Establish the structure of C_4H_8O from its NMR spectrum (Fig. 21).

799*. Establish the structure of $C_5H_{10}O$ that has an intense absorption band at 1720 cm^{-1} in the I-R spectrum and two resonance signals: δ_1 0.9 ppm (triplet) and δ_2 2.4 ppm (quadruplet) in the NMR spectrum.

CHAPTER TWELVE

CARBOXYLIC ACIDS AND THEIR DERIVATIVES

SATURATED MONOBASIC CARBOXYLIC ACIDS

A. Isomerism. Nomenclature. Methods of Preparing

800. Write structural formulas of: (a) propionic acid, (b) butyric acid, (c) isobutyric acid, (d) trimethylacetic acid, (e) valeric acid, (f) palmitic acid, (g) stearic acid. Give their IUPAC names.

801. Name the following acids:

(a) $CH_3-CH(CH_3)-CH_2-COOH$, (b) $(CH_3)_3C-CH_2-COOH$;

(c) $CH_3-\underset{\displaystyle COOH}{\underset{|}{CH}}-CH_2CH_3$

802. Write structural formulas of all isomers of the acid $C_5H_{10}O_2$. Name them.

803. What is known as an acid residue (acyl)? Give formulas and name acyls of formic, acetic, and propionic acids.

804. Obtain propionic acid by oxidation of: (a) alcohol, (b) aldehyde, (c) ethylene hydrocarbon, (d) ketone.

805. Obtain butyric acid by oxo synthesis.

806. Obtain propionic acid and isobutyric acid by the Grignard reaction.

807. What compound is obtained by the following conversion?

$$CH_3CH_2CH_2Br \xrightarrow[\text{heat}]{KCN} \ldots \xrightarrow[H^+]{H_2O} \ldots$$

808. Suggest two methods to synthesize butyric acid from propyl bromide.

809. Obtain propionic acid from ethylene.

810. Complete the following:

$$CH_3CHBrCH(CH_3)CH_2CH_3 \xrightarrow[\text{(alcohol), heat}]{KOH} \ldots \xrightarrow{HBr} \ldots$$

$$\ldots \xrightarrow[\text{abs. ether}]{Mg} \ldots \xrightarrow{CO_2} \ldots \xrightarrow[H^+]{H_2O} \ldots$$

811. Obtain butyric and isobutyric acids from malonic acid.

812*. What compound will be obtained by the following transformations?

$$CH_3-(CH_2)_4-COOH \xrightarrow[H^+]{C_2H_5OH_5} \ldots \xrightarrow[2)\ H_2O]{1)\ 2C_6H_5MgBr} \ldots$$

$$\ldots \xrightarrow{\text{heat}} \ldots \xrightarrow[CrO_3]{\text{oxidation}} \ldots$$

813*. Obtain butyric acid from valeric acid by the Barbier-Wieland reaction.

814. By what method can 4-methyl-2-pentanone be converted: (a) into isovaleric acid, (b) into isobutyric acid?

815. Accomplish the following conversions:

(a) $CH_3CH_2CH(OH)CH(CH_3)_2 \longrightarrow CH_3CH_2-\underset{\displaystyle CH(CH_3)_2}{\underset{|}{CH}}-COOH$

(b) $CH_3-CO-CH_3 \longrightarrow (CH_3)_3C-COOH$

B. Structure. Properties

816. Cryoscopic determination of molecular mass, and also X-ray studies of carboxylic acid crystals have shown that carboxylic acids exist in the form of dimers. How can this fact be explained?

817. Compare the strength of the hydrogen bonds in alcohols and carboxylic acids. What is the cause of this difference?

818. In what region of the I-R spectrum do the absorption bands caused by oscillations of the carboxylic group atoms appear? Can the valence oscillations of the OH group of alcohol and acid (carbonyl group of ketone and acid) be distinguished by the I-R spectrum?

819. Consider the I-R spectrum of butyric acid (liquid film, Fig. 22) and identify as many bands characterizing the atom groups available in the molecule as possible.

820. Describe the modern concept of the structure of the carboxyl group. Explain: (a) the decreased affinity of the $\diagdown C=O$ group for nucleophilic addition reactions, (b) acid $\diagup$ properties of carboxylic acids.

821. What is the measure of acidity of carboxylic acids and how can it be determined?

822. Compare acid properties of the following compounds: (a) ethyl alcohol, formic and butyric acids, (b) butyric, alpha-nitrobutyric, and gamma-nitrobutyric acids. Explain the differences.

823. Arrange the following compounds in the order of their increasing acid properties: (a) $C_2H_5NO_2$,

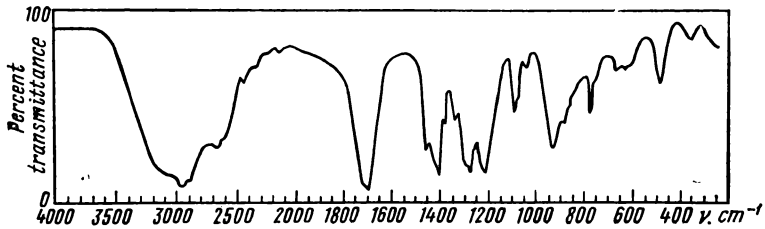


Fig. 22. I-R spectrum of butyric acid

(b) CH_3CH_2COOH, (c) $CH_3CH_2CH_2OH$. Prove your answer by chemical reactions.

824. Explain the different acid properties of the following carboxylic acids:

Acid	HCOOH	CH_3COOH	$ClCH_2COOH$	Cl_3CCOOH
pK_a (25°C)	3.77	4.76	2.86	0.65

825. What reactions are used for quantitative and qualitative determination of carboxylic groups in organic compounds?

826. Titration of 1 g of acetic acid solution requires 20 ml of 0.5 N solution of KOH. Calculate the percentage content of acetic acid in the test solution.

827. What compounds are formed during decarboxylation of the following acids: (a) nitroacetic acid, (b) cyanoacetic acid, (c) trichloroacetic acid? How can the easiness with which carbon dioxide is eliminated from these acids be explained?

828. Write structural formulas for all isomers of the acid $C_6H_{12}O_2$, decarboxylation of which gives methylbutane. Name the acids.

829. What compounds are formed by electrolysis of aqueous solutions of sodium salts of propionic acid? isobutyric acid? Describe the processes occurring at the cathode and anode.

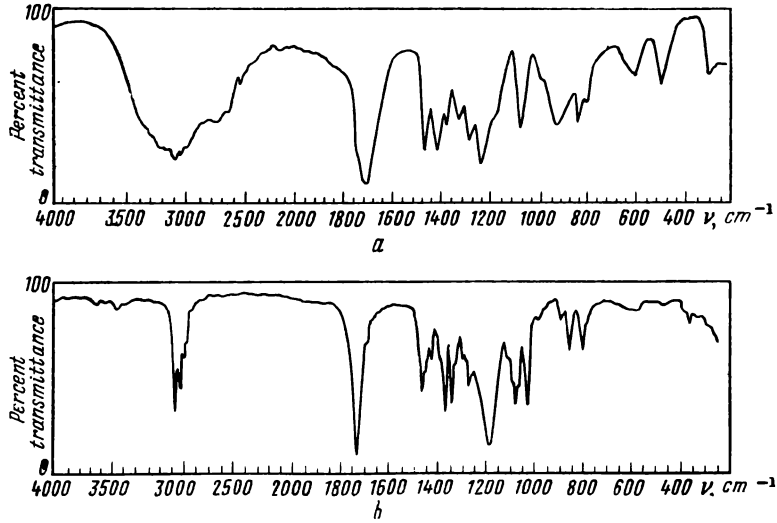


Fig. 23. I-R spectra of propionic acid and ethyl propionate

830. What compound is formed during dry distillation of a calcium salt of butyric acid? a mixture of calcium salts of formic and propionic acids?

831. Obtain: (a) dibutyl ketone, (b) octane, (c) butane, from valeric acid.

832. Using acetic acid, obtain: (a) ethyl acetate, (b) acetyl chloride, (c) acetic anhydride, (d) acetamide.

833. Figure 23 shows the I-R spectra of propionic acid and ethyl propionate (liquid film). Determine which spectrum corresponds to which compound. Indicate characteristic frequencies of carboxyl and ester groups.

834. Write the reaction of butyric acid: (a) with Cl_2 in the light, (b) with excess $LiAlH_4$ and then with water.

835. What reactions can be used to distinguish between the following isomeric acids: $CH_3CH_2CH(CH_3)COOH$ and $(CH_3)_3C—COOH$?

836. Describe the commercial method of preparing formic acid. Give reactions in which the specific properties of formic acid are clearly different from those of the acids belonging to the same homologous series.

837. Describe the commercial method for the manufacture of acetic acid. Indicate uses of the acid.

DERIVATIVES OF SATURATED MONOBASIC CARBOXYLIC ACIDS

838. What compounds are known as functional derivatives of carboxylic acids? Name the following substances:

(a) CH_3COONa, (b) $CH_3—\underset{\displaystyle CH_3}{\underset{|}{CH}}—COOCH_3$, (c) $CH_3CH_2C(=O)—O—C(=O)CH_2CH_3$,

(d) $CH_3CH_2CH_2C(=O)—O—Ca—O—C(=O)CH_3$, (e) $CH_3CH_2CH_2COCl$,

(f) $CH_3CH_2CONH_2$, (g) CH_3CN

What property is common with all derivatives of carboxylic acids?

839. Name the following compounds and write the reactions by which they are produced:

(a) CH_3CH_2COONa, (b) $(CH_3CH_2CH_2COO)_2Ba$

(c) CH_3CH_2COOAg, (d) $CH_3—CH(CH_3)—COONH_4$

840. Compare the electronic structure of the carboxyl group and carboxylate anion. Where is the conjugation effect stronger?

841. Obtain acetyl chloride from acetic acid by all known methods.

842. Illustrate the use of chlorides of carboxylic acids in the O- and N-acylation, using the reaction between acetyl chloride and water, methyl alcohol, ammonia and methylamine as an example. Consider the reaction mechanisms. Name the products obtained.

843. Write the reactions of butylamine: (a) with CH_3COCl, (b) with CH_3CH_2Cl. Compare the mechanisms of the reactions.

844*. Write the reaction of acetyl chloride with ethylmagnesium bromide (molar ratio 1 : 1). Explain why the activity of acid halides toward the Grignard reagent decreases in the series $R{-}COF > R{-}COCl > RCOBr$.

845. How can bromoacetic acid be distinguished from its bromoacetyl bromide by chemical and spectral methods?

846. Obtain alpha-bromopropionyl bromide from ethylene.

847. Accomplish the following transformations:

$$CH_3CH_2COOH \xrightarrow{SOCl_2} \ldots \xrightarrow[\text{abs. ether}]{2CH_3MgI} \ldots \xrightarrow[H^+]{H_2O} \ldots$$

848. Obtain propionic anhydride: (a) from propionic acid, (b) from sodium propionate.

849. Obtain acetopropionic anhydride from acetylene and inorganic reagents.

850. Write reactions of propionic anhydride with water, ethyl alcohol, ammonia, and ethylamine. Name the obtained products. Consider the reaction mechanisms.

851. What compounds are formed by the following transformations?

$$CH_3COCH_3 \xrightarrow{700\ ^\circ C} \ldots \xrightarrow{CH_3COOH} \ldots \xrightarrow{(CH_3CH_2)_2NH} \ldots$$

852. Describe industrial methods for preparing acetic anhydride and its industrial uses.

853. Write the reaction of esterification of propionic acid with methyl alcohol. Consider the reaction mechanism.

854*. Explain the following: (a) most carboxylic acids fail to be esterified unless a strong mineral acid is added, (b) high concentration of a mineral acid produces an 'anticatalytic' effect, and the rate of esterification sharply decreases.

855*. Arrange the following acids in the order of their increasing rate of esterification by methyl alcohol: (a) acetic acid, (b) trimethylacetic acid, (c) propionic acid. Explain.

856. Obtain methyl propionate by acylation of alcohol with acid chlorides, and also with acid anhydrides. Consider the reaction mechanisms. Which of these compounds and why is a stronger acylating agent?

857. Obtain methyl propionate using the following methylating agents: (a) CH_3OH, (b) CH_2N_2, (c) CH_3I.

858. Obtain isopropyl isobutyrate from propyl bromide and inorganic reagents.

859. Write the reaction of alkaline hydrolysis of methyl propionate. Consider its mechanism.

860. Compare the conditions of hydrolysis of the following compounds: (a) acetyl chloride, (b) acetic anhydride, (c) ethyl acetate. Explain the differences in the reactivity of these compounds.

861. Write the following reactions for methyl propionate: (a) hydrolysis, (b) alcoholysis (with propyl alcohol), and (c) ammonolysis. Specify the prerequisite conditions.

862. Write the reaction of preparing isoamyl butyrate from ethyl butyrate by transesterification.

863. Arrange the following compounds in the order of their decreasing acylating power: (a) $(CH_3CO)_2O$, (b) CH_3COOH, (c) CH_3COCl, and (d) $CH_3COOC_2H_5$. Explain.

864. Complete the following:

$$CH_3CH_2COOH \xrightarrow{PCl_5} \ldots \xrightarrow{C_2H_5OH} \ldots \xrightarrow{2CH_3MgBr} \ldots$$

$$\ldots \xrightarrow[H+]{H_2O} \ldots \xrightarrow{(CH_3CO)_2O} \ldots \xrightarrow[H_2O]{NH_3} \ldots$$

865. Write the reaction equations of ethyl butyrate: (a) with Na + C_2H_5OH, (b) with $LiAlH_4$ (ether), (c) with H_2 (copper-chromium catalyst, heat, pressure).

866. Can the following compounds be distinguished by their I-R spectra?

(a) $CH_3CH_2-COOCH_3$ and $CH_3CH_2CH_2COOH$

(b) $CH_3CH_2-COOCH_3$ and $CH_3CH_2-CO-CH_3$

867. Obtain acetamide: (a) by acylation of ammonia, (b) from an ammonium salt of a carboxylic acid, (c) from a nitrile.

868. Suggest a method for preparing isobutyramide from propylene.

869*. Suggest a method for preparing dimethylacetamide from acetylene and dimethylamine.

870. Consider the structure of a molecule of acetamide. Explain the cause of amphoteric properties of carboxylic acid amides.

871. What compound can be obtained by reducing isobutyramide with $LiAlH_4$. Write a balanced equation of the reaction. Compare the basic properties of the starting substances and products.

872. Write the reaction of propylamine with acetyl chloride. Compare the basic properties of the starting and the end products. Explain.

873. Arrange the following compounds in the order of their increasing basic properties: (a) methylamine, (b) acetamide, (c) tetramethylammonium hydroxide, (d) N-methylacetamide. Explain.

874. Write the following reactions for butyramide: (a) hydrolysis, (b) dehydration, (c) reaction with HNO_2.

875. Obtain ethylamine from propionamide. Consider the mechanism of the Hofmann rearrangement.

876. Accomplish the following conversions:

$$(CH_3)_2CH-COOH \xrightarrow{NH_3(H_2O)} \ldots \xrightarrow{heat} \ldots$$

$$\ldots \xrightarrow[NaOH]{NaOCl} \ldots \xrightarrow{CH_3COCl} \ldots$$

Name the starting, intermediate and end products.

877*. Dimethylformamide is often used as a polar solvent in organic reactions. Characterize its effect on the rate of nucleophilic substitution reactions (S_N1 and S_N2) with alkyl halides.

878*. Write the reaction of propyl bromide with KCN in an aqueous alcohol. What side product is formed in the reaction? Consider the mechanism of the reaction.

879*. How will the ratio of the reaction products in the previous problem change if: (a) silver cyanide is substituted for KCN, (b) dimethylformamide is used as a reaction medium instead of water and alcohol?

880. Obtain propionitrile by all known methods. Write the reaction equations for its reduction and hydrolysis.

881*. What compounds are formed by the reaction of butyronitrile with the following substances: (a) aqueous solution of alkali with heating, (b) $LiAlH_4$, (c) CH_3CH_2MgBr (absolute ether), (d) C_2H_5OH (H^+, H_2O).

882. Write the synthesis of ethylcarbylamine: (a) from ethyl iodide, (b) from ethylamine.

883. Using ethylcarbylamine, consider the structure of isonitriles and their chemical properties (reduction, hydrolysis).

884. By what reactions can the following isomers be distinguished: $CH_3CH_2CH_2CN$ and $CH_3CH_2CH_2NC$?

885. Obtain *n*-propylamine and *n*-amylamine from *n*-butyl alcohol.

UNSATURATED MONOBASIC CARBOXYLIC ACIDS

886. Write structural formulas of acrylic, crotonic, oleic, and propargylic acids. Give their IUPAC names.

887. Write structural formulas of all isomers of the acid $C_4H_6O_2$. Which of them will have geometric isomers?

888. Oleic and elaidic acids have the structural formula $CH_3(CH_2)_7CH=CH(CH_2)_7COOH$. On what does the difference in their physical properties depend (oleic acid melts at +14°C and elaidic at 51-52°C)?

889. Figure 24 shows U-V spectra of acetic and crotonic acids (in dilute H_2SO_4). Identify the curves. Explain the observed differences in their ultra-violet spectra.

890*. Figure 25 shows the NMR spectrum of ethyl methacrylate. Establish to which protons the resonance signals correspond.

891. Describe industrial methods of manufacturing acrylic and methacrylic acids. Indicate their commercial uses.

892. What compounds are formed by the reaction of acrylic acid with Na_2CO_3, Br_2, HBr? Consider the mechanism of the latter reaction. What compounds can be obtained by the oxidation of acrylic acid?

893. Obtain propargylic acid from acetylene. Compare the acid properties of propargylic and acetic acids.

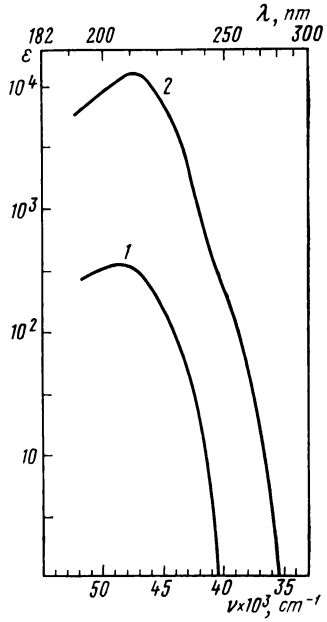


Fig. 24. U-V spectra of acetic and crotonic acids

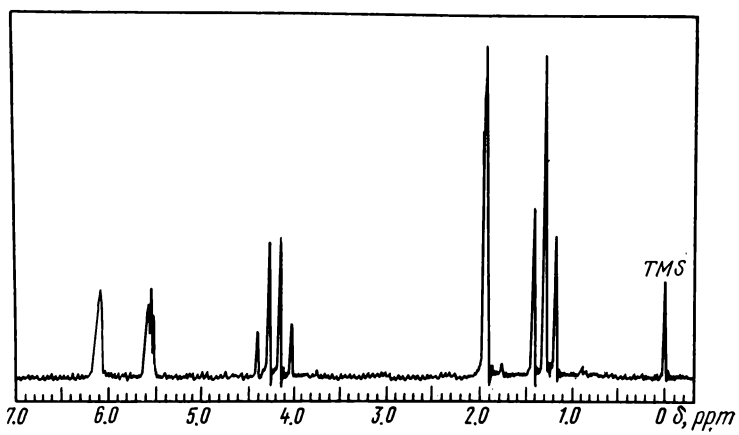


Fig. 25. NMR spectrum of ethyl methacrylate

894*. What spectral methods should be used to distinguish between the following compounds given in pairs?

(a) $CH_2=CH-CH_2COOH$ and $CH_3-CH=CH-COOH$

(b) $CH_2=CH-COONH_4$ and $CH_2=CH-CONH_2$

(c) $HC\equiv C-COOCH_3$ and $CH_2=CH-COOCH_3$

895. What carboxylic acids are formed by hydrolysis of fats? Write structural formulas of glycerides of stearic and oleic acids.

DICARBOXYLIC ACIDS

896. Write structural formulas of oxalic, malonic, methylmalonic, and adipic acids, succinic anhydride, adipamide, a potassium salt of acid ester of succinic acid.

897. Name the following compounds: (a) $HOOC-CONH_2$, (b) $NaOOC-(CH_2)_4-COOC_2H_5$, (c) $NC-(CH_2)_4-CN$. Obtain them from the corresponding dicarboxylic acids.

898*. Obtain diethyl succinate from a potassium salt of an acid malonate ester.

899*. Obtain adipic acid from succinic acid.

900*. Explain why lower dicarboxylic acids are stronger than monocarboxylic acids. How can it be explained that pK_a^2 of dicarboxylic acids is lower than pK_a of monocarboxylic acids (except pK_a^2 of oxalic acid)?

901*. Esterification of oxalic and also formic acids does not require a mineral acid as a catalyst. Explain.

902. Compare the attitude to heat of oxalic, malonic, succinic, glutaric, and adipic acids. Write the reactions. Name the obtained compounds.

903. Write the synthesis of malonic acid from acetic acid. On what does the easiness with which malonic and alkylmalonic acids are decarboxylated depend?

904. Malonic ester is obtained by the action of ethanol and a mineral acid on a salt of cyanoacetic acid. Fill in the formulas of intermediate products into the following:

$$NCCH_2-COONa \xrightarrow[(H^+)]{C_2H_5OH} \ldots \xrightarrow[(H^+)]{C_2H_5OH} \ldots$$

$$\ldots \xrightarrow{H_2O} C_2H_5OOC-CH_2-COOC_2H_5$$

905*. Consider the structure of malonic ester. Write the reaction of the ester with the following compounds: (a) H_2O (H^+) with heating, (b) Na in alcohol, (c) CH_3CHO (in the presence of a base), (d) HNO_2.

906. Obtain sodiomalonic ester. Consider its structure and chemical properties.

907*. Write the reaction of sodiomalonic ester with: (a) CH_3CH_2Br, (b) $ClCH_2COOC_2H_5$, (c) I_2.

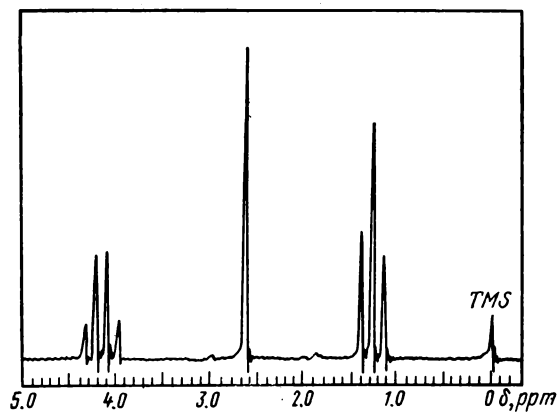


Fig. 26. NMR spectrum of $C_8H_{14}O_4$

908. Write the synthesis of butyric acid from malonic ester.

909. Obtain dimethylacetic acid using malonic ester.

910*. What is the structure of the compound $C_8H_{14}O_4$ if it was obtained as follows:

$$CH_2(COOC_2H_5)_2 \xrightarrow{C_2H_5ONa} \ldots \xrightarrow{ClCH_2COOC_2H_5} \ldots \xrightarrow[\text{heat}]{H_2O\ (H^+)} \ldots \xrightarrow[(H^+)]{2C_2H_5OH} C_8H_{14}O_4$$

and has the NMR spectrum shown in Fig. 26?

911*. Prepare crotonic acid from malonic ester.

912. What is the commercial process for the manufacture of adipic acid? Indicate its industrial uses.

913. Draw formulas of geometric isomers of sym-ethylenedicarboxylic acid. Name them.

914. Compare stability of *cis*- and *trans*-isomers of ethylenedicarboxylic acid. In what conditions does *cis*-isomer convert into *trans*-isomer and vice versa (*cis-trans*-isomerism)?

915. Compare heats of combustion of fumaric and maleic acids, and also their acid properties. Which of the acids can give anhydride? Develop your reasons.

916. Give examples of uses of maleic anhydride in diene synthesis.

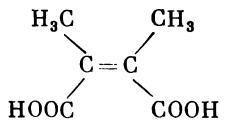
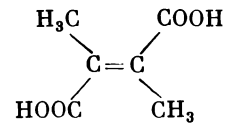
917. What reactions can be used to distinguish between the following compounds:

(a) $HCOOH$ and CH_3COOH

(b) $CH_3COOC_2H_5$ and CH_3-O-CH_2COOH

(c) $CH_2=CH-COOH$ and CH_3CH_2COOH

(d) CH_3COBr and $BrCH_2COOH$

(e)  and 

(f) $HC\equiv C-COOC_2H_5$ and $CH_2=CH-COOC_2H_5$

(g) CH_3COONH_4 and CH_3CONH_2

(h) $(CH_3CO)_2O$ and $CH_3COOC_2H_5$

918. Write structural formulas of compounds having the following properties: (a) an unsubstituted carboxylic acid that gives the silver mirror reaction, (b) a carboxylic acid that does not require a catalyst for its esterification, (c) a saturated dicarboxylic acid that gives a cyclic ketone on heating with $Ba(OH)_2$, (d) an unsaturated dicarboxylic acid giving an inner anhydride on heating.

C. Establishing the Structure of Organic Compounds by Their Properties

919. Write a structural formula of a substance having the composition $C_3H_6O_2$, the I-R spectrum of which has a wide band of absorption at 2700-2500 cm^{-1}, and an intense band of absorption at 1710 cm^{-1}.

920. Establish the structure of the compound $C_4H_8O_2$ having the following properties: (a) it reacts with an aqueous

solution of soda with liberation of CO_2, (b) when fused with alkali it gives propane, (c) with $Ca(OH)_2$ it gives $C_8H_{14}O_4Ca$, the pyrolysis of which gives diisopropyl ketone.

921*. A substance having the composition $C_7H_{14}O_2$ reacts with alkalis to give salts; when heated with NaOH it turns into the hydrocarbon C_6H_{14} that can be obtained also by electrolysis of a salt of isobutyric acid. The substance in question reacts with bromine (in the presence of catalytic quantities of phosphorus) to give $C_7H_{13}BrO_2$. Establish the structure of $C_7H_{14}O_2$.

922. The substance $C_4H_{10}O_4$ reacts with acetic anhydride to give a derivative having the composition $C_{12}H_{18}O_8$. How many hydroxyls are contained in the original substance? What is its structure?

923*. The substance $C_6H_{10}O_3$ is decomposed by ammonia (1 mole) into two products, viz., $C_3H_6O_2$ (I) and C_3H_7NO (II). The compound (II) is hydrolyzed to give the compound (I). Determine the structure of the substance $C_6H_{10}O_3$.

924*. Establish the structure of the compound $C_6H_{13}NO$ the hydrolysis of which gives dimethylamine and a substance having the formula $C_4H_8O_2$. The I-R spectrum of the latter gives characteristic absorption bands at 2700-2500 and 1705 cm^{-1} and can be obtained by oxidation of isobutyl alcohol.

925. Write a structural formula of a substance having the composition C_2H_3N that is hydrolyzed into formic acid and reduced into dimethylamine.

926*. Determine the structure of the compound C_4H_9NO that gives C_4H_7N on heating with P_2O_5. The latter substance is reduced with sodium metal in alcohol to give the amine $C_4H_{11}N$ which is completely methylated with subsequent decomposition of a quaternary ammonium base to give 1-butene.

927*. Establish the structure of C_4H_7ClO the alkaline hydrolysis of which gives the salt $C_4H_7O_2Na$. It reacts with ethylamine to give $C_6H_{13}NO$. The latter is reduced with $LiAlH_4$ to give ethyl-*n*-butylamine.

928*. The substance C_4H_7N does not form salts with acids. When heated with an aqueous alkali, it gives the compound $C_4H_7O_2Na$, which is electrolyzed to give 2,3-dimethylbutane. The NMR spectrum of the substance has two

resonance signals: δ_1 1.3 ppm (doublet), and δ_2 2.7 ppm (multiplet).

929. Establish the structure of the compound C_4H_9NO that reacts with bromine and an alkali to give C_3H_9N. The latter reacts with nitrous acid to give mainly isopropyl alcohol.

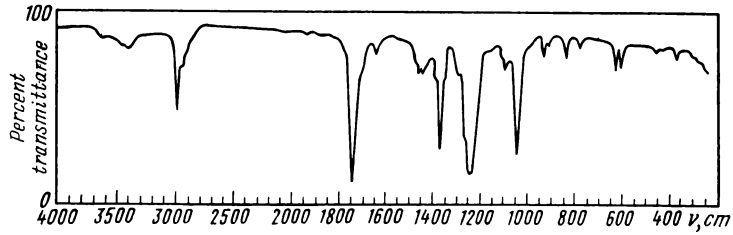


Fig. 27. I-R spectrum of $C_4H_8O_2$

930. Determine the structure of a neutral compound having the formula $C_{10}H_{18}O_4$ the hydrolysis of which gives an acid substance having the composition $C_6H_{10}O_4$. When reduced

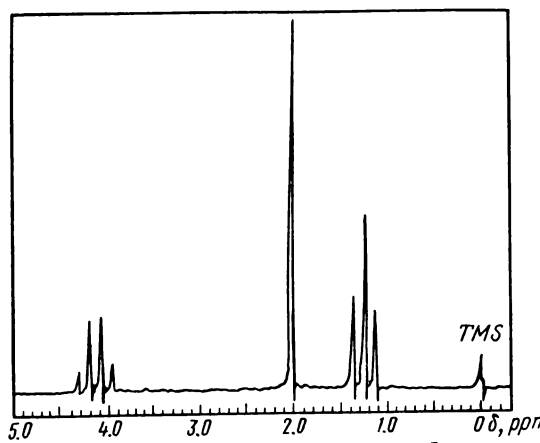


Fig. 28. NMR spectrum of $C_4H_8O_2$

with $LiAlH_4$, the substance converts into 1,6-hexanediol and ethyl alcohol.

931. Determine the structure of the substance $C_4H_6O_2$ that reacts with sodium bicarbonate to liberate CO_2

and on ozonolysis gives formaldehyde and pyruvic acid ($CH_3COCOOH$).

932. What is the structure of the substance $C_4H_4O_2$ that reacts with alkalis to give salts and produces a characteristic precipitate on reaction with ammoniacal cuprous oxide?

933. A neutral substance $C_7H_{12}O_4$ reacts with sodium metal to liberate hydrogen and form $C_7H_{11}O_4Na$. The latter reacts with propyl iodide, with subsequent hydrolysis, to give valeric acid. What is the structural formula of the substance $C_7H_{12}O_4$?

934. A substance having the formula $C_6H_8O_4$ decolourizes bromine water, during ozonolysis gives pyruvic acid as the only product, and when heated, decomposes into water and anhydride $C_6H_6O_3$. Determine the structure of the substance.

935*. Determine the structure of the compound $C_4H_8O_2$ from its I-R (liquid film) and NMR spectra (Figs. 27 and 28).

CHAPTER THIRTEEN

HALOGEN-SUBSTITUTED ACIDS. HYDROXY ACIDS. AMINO ACIDS

HALOGEN-SUBSTITUTED ACIDS

936. Write structural formulas of all monobromovaleric acids having the normal chain of carbon atoms. Name them according to the IUPAC system.

937. Write structural formulas of the following compounds: ammonium salt of β-chlorobutyric acid, ethyl chloroacetate, alpha-bromobutyramide, alpha-chloropropionyl chloride, gamma-bromovaleronitrile.

938. What compounds can be obtained by the action of chlorine on acetic acid? What is the mechanism of the reactions?

939. Obtain alpha-bromopropionic acid from propionic acid by the Hell-Volhard-Zelinsky method. Give probable reaction mechanism.

940*. Explain why chlorine acts on propionic acid in the light to give a mixture of alpha- and beta-chloropropionicacids.

941. Obtain beta-bromopropionic acid, beta-bromobutyric acid from acrylic and crotonic acids respectively. Consider the mechanisms of the reactions.

942. Write the synthesis of ω-chlorovaleric acid using the telomerization reaction of ethylene with carbon tetrachloride.

943*. Accomplish the following conversions:

(a) $CH_2=C=O \longrightarrow ClCH_2COOH$

(b) $CH_3CH_2OH \longrightarrow Cl_3C-COOH$

(c) $CH_3CH_2COOH \longrightarrow CH_3-CHI-COOH$

(d) $CH_3-CHO \longrightarrow CH_3-CHBr-CH_2-COOH$

(e) $CH_2=CH-CH_3 \longrightarrow CH_2Br-CHBr-COOH$

944. Arrange the following acids in the order of their increasing acid properties:

(a) $CH_2ClCOOH$, CH_3COOH and CCl_3COOH

(b) $CH_3CHBrCH_2COOH$, $CH_2BrCH_2CH_2COOH$ and $CH_3CH_2CHBrCOOH$

(c) $CH_2ClCOOH$, $CH_2BrCOOH$, CH_2FCOOH, CH_2ICOOH

Develop your reasons.

945. Write the reactions of alpha-bromopropionic acid with H_2O, KI, NH_3, KCN, and C_2H_5ONa. Explain the increased activity of the halogen of α-bromopropionic acid in nucleophilic substitution reactions.

946. What compounds can be obtained by the following reactions?

(a) $CH_3CHClCOOH + C_2H_5OH \xrightarrow{(H^+)} \ldots$

(b) $CH_2ClCOOH + PCl_5 \longrightarrow \ldots$

947*. Fill in the structural formulas of the intermediate and end products:

$$H-C\equiv C-H \xrightarrow[Hg^{2+},\ H^+]{H_2O} \ldots \xrightarrow{O_2} \ldots \xrightarrow[(h\nu,\ \text{heat})]{2Cl_2} \ldots \xrightarrow[H^+]{C_2H_5OH} \ldots$$

Compare the structure of the obtained compound with the NMR spectrum: δ_1 1.35 ppm (triplet), δ_2 4.33 ppm (quartet) and δ_3 5.93 ppm (singlet).

948. Write the conversions occurring during heating of alpha-, beta-, and gamma-chlorovaleric acids. Name the obtained compounds.

HYDROXY ACIDS

949. Name the following compounds:

(a) $CH_3CH(OH)CH_2COOH$, (b) $CH_3CHCH_2CH_2-CO$ (O bridge)

(c) $CH_2CH_2CH_2-CO$ (O bridge), (d) $CH_3-CH(OCH_3)-COOH$

(e) $CH_3CH_2CH(OH)-COOCH_3$, (f) $CH_2(OH)-CONH_2$

950. Write structural formulas of lactic acid, tartaric acid, beta-hydroxybutyramide, gamma-valerolactone, and delta-valerolactone.

951. Obtain lactic acid by all known methods.

952. Obtain alpha-hydroxybutyric acid: (a) from propionic aldehyde, (b) from alpha-chlorobutyric acid, (c) from alpha-aminobutyric acid.

953. Write the reaction of preparing ethyl β-hydroxyvalerate by the Reformatsky reaction.

954*. What compound is formed by the Reformatsky reaction from gamma-methyl bromocrotonate and acetaldehyde?

955. Suggest a method for preparing tartaric acid from ethylene.

956. Complete the following:

$$CH_3CH_2CH_2COOH \xrightarrow{Ca(OH)_2} \ldots \xrightarrow{\text{heat}} \ldots \xrightarrow{HCN} \ldots$$
$$\ldots \xrightarrow[(H^+),\ \text{heat}]{2H_2O} \ldots$$

957. Arrange the following acids in the order of their increasing acid properties: glycolic, acetic, and chloroacetic acids. Develop your reasons.

958. Write the reaction of glycolic acid with: (a) PCl_5, (b) HBr, and (c) HI.

959. Using hydroxybutyric acids as an example, characterize the action of heat on alpha-, beta-, and gamma-hydroxy acids. Name the obtained products.

960*. What compounds are formed by heating: (a) lactic acid, (b) alpha-hydroxyisobutyric acid, with dilute acids?

961. Write the reactions of gamma-butyrolactone and delta-valerolactone with aqueous solution of alkali with heating. What products are formed by the action of mineral acids on the obtained compounds?

962. By what reactions can methyl glycolate be distinguished from methoxy acetic acid?

963. Accomplish the following conversions:

$$CH_3CH=CH_2 \xrightarrow[400°C]{Cl_2} \ldots \xrightarrow[\text{benzoyl peroxide}]{HBr} \ldots \xrightarrow[\text{heat}]{KCN\ (1\ \text{mole})} \ldots$$
$$\ldots \xrightarrow[(H^+)\ \text{heat}]{2H_2O} \ldots \xrightarrow[OH^-]{H_2O} \ldots \xrightarrow[H^+]{\text{heat}} \text{lactone}$$

AMINO ACIDS

964. Write structural formulas of the following compounds: beta-aminobutyric acid, hydrochloride of gamma-ethyl aminovalerate, alpha-aminopropionamide.

965. Name the following compounds:

(a) $CH_3-\underset{\displaystyle NHCH_3}{\underset{|}{CH}}-COOH$, (b) $HOOC-\underset{\displaystyle NH_2}{\underset{|}{CH}}-CH_2CH_2-COOH$

(c) $CH_3CH_2-\underset{\displaystyle NHCOCH_3}{\underset{|}{CH}}-COOH$, (d) $CH_3-\underset{\displaystyle NH_3^+Br^-}{\underset{|}{CH}}-CH_2COOC_2H_5$

(e) $H_2N-CH_2CH_2CH_2-CONH_2$

966. Obtain alpha-aminopropionic acid from the corresponding alpha-halogen-substituted acid. What side products are formed in this process?

967. Write the reactions of preparing alpha-aminobutyric acid from the corresponding aldehyde: (a) by cyanohydrin synthesis, (b) by cyanohydrin synthesis modified by Zelinsky and Stadnikov.

968. Obtain beta-aminobutyric acid by the Rodionov reaction.

969. omega-Aminoenanthic acid, $H_2N-(CH_2)_6-COOH$, is used in the manufacture of synthetic fibre 'enanth'. Write the reaction for preparing the acid using the telomerization reaction of ethylene with carbon tetrachloride.

970. Consider the structure of alpha-amino acids using aminoacetic acid as an example. What is a bipolar ion? How can the high temperatures at which amino acids melt and also their insolubility in ordinary organic solvents be explained?

971. Write the reactions characterizing the amphoteric properties of amino acids.

972. Explain why in the presence of mineral acids, amino acids in an aqueous medium move toward the cathode and in an alkaline medium toward the anode. What is the isoelectric point?

973. Write the reaction of alpha-aminopropionic acid with C_2H_5OH (in the presence of HCl). Compare the basic properties of the starting and the end products. Explain.

974. Obtain N-acetyl derivative by all known methods using aminoacetic acid. Compare the acid properties of the starting and the end products.

975. What compounds are formed by the action of aminoacetic acid on C_2H_5I?

976. Write the reaction of alpha-aminopropionic acid with HNO_2. Characterize the importance of the reaction of amino acids with nitrous acid in the analysis of organic compounds.

977. The action of nitrous acid on 0.4 g of a mixture containing alanine gives 44.8 cc of nitrogen. Determine the percentage content of alanine in the test mixture.

978. Compare the chemical properties, dependent on the presence of the amino group, in the following compounds: ethylamine, acetamide, aminoacetic acid.

979. Characterize the attitude of alpha-, beta-, and gamma-amino acids to heat. Name the formed products.

980. Compare the attitude of alpha-, beta-, and gamma-chloro-, hydroxy- and amino-substituted valeric acids to heat. Name the products formed.

981. Indicate industrial uses of lactam of ε-aminocaproic acid (caprolactam).

Establishing the Structure of Organic Compounds by Their Properties

982. Establish the structure of $C_4H_7ClO_2$ that reacts with aqueous solution of soda with liberation of carbon dioxide, and easily eliminates hydrogen chloride on heating.

983. A substance having the composition $C_5H_{10}O_3$ is heated to give $C_5H_8O_2$. The latter is oxidized into a mixture of propionic and oxalic acids. What is the structure of the original compound?

984. Establish the structure of $C_4H_6O_2$ that does not react with bromine water or sodium bicarbonate solution. When heated with an aqueous solution of sodium hydroxide it turns into a salt having the composition $C_4H_7O_3Na$.

985*. A substance having the composition $C_6H_{13}NO_2$ does not react with sodium bicarbonate or nitrous acid, but easily reacts with hydrochloric acid to give a salt. When heated with an aqueous solution of alkali, it turns into a salt having the composition $C_4H_8NO_2Na$. Determine the structure of the test substance.

986*. Determine the structure of the compound $C_3H_5ClO_2$ that reacts with an aqueous solution of soda to liberate CO_2. The NMR spectrum of the compound has the following re-

sonance signals: δ 1.73 (doublet), 4.47 (quartet) and 11.22 (singlet), in parts per million, with respect to tetramethylsilane.

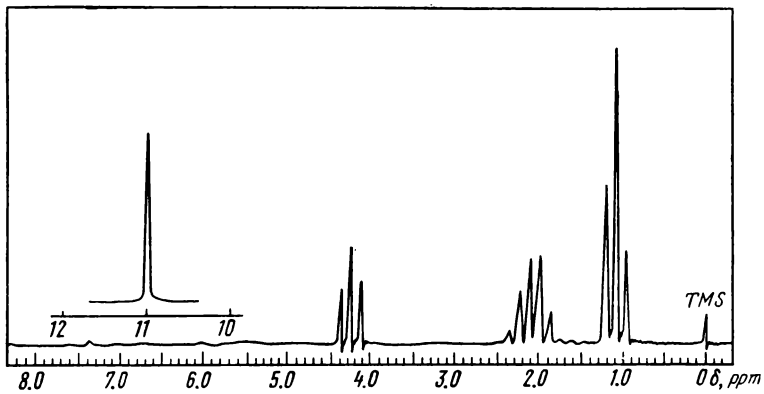


Fig. 29. NMR spectrum of $C_4H_7BrO_2$

987*. Figure 29 gives NMR spectrum of a substance having the composition $C_4H_7BrO_2$. The I-R spectrum of this compound has a wide absorption band in the region of 3100-2800 cm^{-1}, and an intense absorption band at 1720 cm^{-1}. Establish the structure of the compound $C_4H_7BrO_2$.

CHAPTER FOURTEEN

ALDEHYDO AND KETO ACIDS. ACETOACETIC ESTER

A. Isomerism. Nomenclature

988. Write structural formulas of the simplest aldehydo acid, alpha-, beta-, and gamma-keto acids. Name them.

989. Name the following compounds:

(a) $C_2H_5OOC-CHO$

(b) $CH_3-CO-CH_2-COOC_2H_5$

(c) $CH_3CO-CH(CH_3)-COOCH_3$

(d) $CH_3-CO-CH_2CH_2CH_2-COOH$

990. Write structural formulas of the following compounds: (a) pyruvonitrile, (b) isopropyl acetoacetate, (c) dimethyl acetoacetic ester, (d) ethyl formylacetate, (e) oxime of gamma-ketovaleric acid.

991. Write structural formulas of the simplest monoketo dicarboxylic acid, which is: (a) alpha- and beta-keto acid at the same time, (b) beta-keto acid only. Name these compounds.

B. Methods of Preparing

992. Obtain glyoxylic acid from: (a) acetic acid, (b) ethylene glycol.

993. Suggest a method for synthesis of pyruvic acid using the following starting substances: (a) acetic acid, (b) propionic acid.

994. Obtain acetoacetic ester from ethyl acetate. Consider the mechanism of the reaction.

995. Write the reaction of ester condensation of ethyl propionate. Name the compound formed.

996*. Obtain: (a) isopropyl acetoacetate, (b) alpha-*n*-ethyl butyryl butyrate, from the corresponding esters of monocarboxylic acids.

997*. Consider the mechanism of the Claisen ester condensation in the general form and answer the following:

(1) why should strong bases, e.g. alkoxides of alkali metals, be used as condensation agents?

(2) why does the reaction of ester condensation occur if all intermediate steps are reversible and the equilibrium is strongly shifted to the left?

(3) why does the yield of beta-keto ester increase if alcohol is distilled or if sodium alkoxide is replaced by stronger condensation agents ($NaNH_2$, NaH)?

998*. What compounds can be formed by heating a mixture of ethyl acetate and ethyl propionate in the presence of sodium ethoxide?

999*. Write the reaction of ester condensation of diethyl oxalate with ethyl acetate. Consider the mechanism of the reaction.

1000. Write the reaction used for commercial manufacture of acetoacetic ester from diketene.

C. Properties

1001. Write the reactions between glyoxylic acid and the following: (a) sodium bisulphite, (b) hydrocyanic acid, (c) hydroxylamine, (d) ammoniacal silver oxide solution.

1002. What substances are formed by the action of caustic alkali on glyoxylic acid (Cannizzaro reaction)?

1003. Give three examples of the reaction of pyruvic acid with the carbonyl, and three reactions with the carboxyl group.

1004. Write the reactions of: (a) decarboxylation, (b) decarbonylation, (c) oxidation of pyruvic acid.

1005. Using acetoacetic acid as an example, explain why beta-keto acids are easy to decarboxylate.

1006. Complete the following:

$$CH_2(COOC_2H_5)_2 \xrightarrow{C_2H_5ONa} \ldots \xrightarrow{CH_3CH_2COCl} \ldots \xrightarrow[\text{heat}]{H_2O,\ (H^+)} \ldots$$

1007*. Consider the I-R spectrum of acetoacetic ester (liquid film, Fig. 30). Determine to what groups do the following wavelengths correspond: 1740, 1715, 1650, and 1630 cm^{-1}. Explain why these frequencies disappear and 1662 cm^{-1} appears instead, if acetoacetic ester is treated with sodium ethoxide in ethyl alcohol.

1008. Write the formulas of keto and enol forms of acetoacetic ester. How can the presence of these tautomeric forms

in acetoacetic ester be proved? How can the enol form be determined quantitatively?

1009. Write the reactions of acetoacetic ester with the following compounds: (a) $NaHSO_3$, (b) NH_2OH, (c) HCN, (d) CH_3COCl (in the presence of pyridine), (e) bromine water, (f) CH_3MgI.

1010. Explain the following. As a drop of $FeCl_3$ is added to an aqueous solution of acetoacetic ester, the solution turns

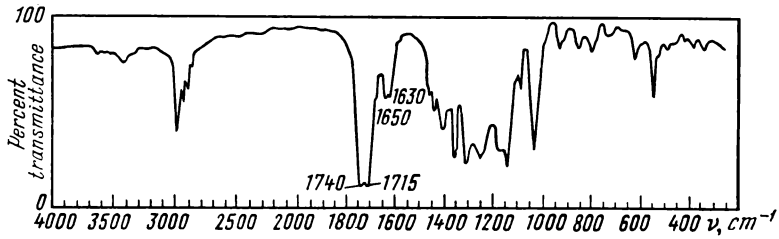


Fig. 30. I-R spectrum of acetoacetic ester

violet. As bromine water is then added, the colour vanishes, but soon reappears. Repeated addition of bromine water causes only transient discolouration.

1011. How can the keto and enol forms of acetoacetic ester be separated? Why does the enol form boil at lower temperatures than the keto form?

1012*. Give the *cis-* and *trans*-configurations of the enol form of acetoacetic ester. Which of them is more energetically advantageous? Why?

1013. Consider the mechanism of the interconversion of the enol and keto forms of acetoacetic ester: (a) under the action of bases, (b) under the action of acids.

1014. Which of the following compounds can exist in the enol form: (a) ethyl acetoacetic ester, (b) dimethyl acetoacetate, (c) alpha-ethyl propionylpropionate? Develop your reasons.

1015. What factors determine the position of tautomeric equilibrium in beta-dicarboxylic compounds. Evaluate qualitatively the degree of enolization of the following compounds: (a) diethyl malonate, (b) ethyl acetoacetate, (c) acetylacetone. Develop your reasons.

1016. Arrange the following compounds in the order of their increasing degree of enolization: (a) acetone, (b) acetoacetic ester, (c) acetylacetone, (d) diacetyl. Develop your reasons.

1017*. Figure 31 shows the NMR spectrum of acetylacetone (pure liquid). Explain the appearance of four resonance signals. Determine to what protons they belong.

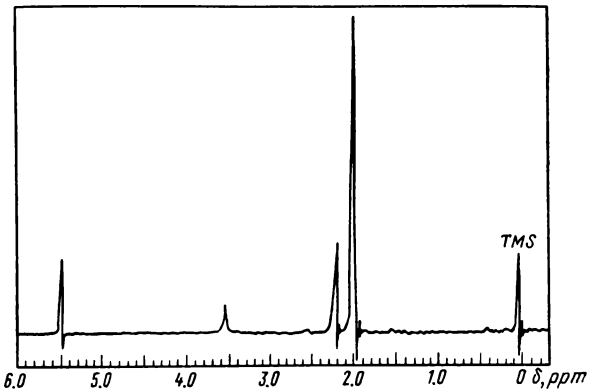


Fig. 31. NMR spectrum of acetylacetone

1018. Write the reaction for preparing sodium acetoacetic ester. Consider the structure of this compound and characterize its reactivity. Give examples of reactions in which the dual reactivity of the ester is manifested.

1019. Write the alkylation reaction of sodium acetoacetic ester with ethyl bromide. Consider the mechanism of the reaction.

1020. Using acetoacetic ester, obtain the following: (a) isopropyl acetoacetic ester, (b) *n*-butyl acetoacetic ester, (c) allyl acetoacetic ester.

1021. What is obtained by adding sodium ethoxide to a mixture of methyl acetoacetic ester and methyl iodide? Write the reaction. Consider its mechanism.

1022. Write the reaction for preparing methylethyl acetoacetic ester using ethyl acetate as the starting compound.

1023*. Write the reaction of propionyl chloride with acetoacetic ester in the presence of pyridine.

1024*. Indicate what main products are formed in the following reactions:

(a) $CH_3COCH_2COOC_2H_5 \xrightarrow{C_2H_5ONa} \ldots \xrightarrow{CH_3OCH_2Cl} \ldots$

(b) $CH_3COCH_2COOC_2H_5 \xrightarrow{C_2H_5ONa} \ldots \xrightarrow{Cl-COOC_2H_5} \ldots$

Develop your reasons.

1025*. Write the reactions of acetoacetic ester with acetyl chloride: (a) in the presence of sodium ethoxide, (b) in the presence of pyridine.

1026. What conversions does acetoacetic ester undergo during heating with a dilute acid? Write the reaction equation. Develop your reasons.

1027. Indicate what products are formed by the action of dilute mineral acid on the following compounds:

(a) $CH_3COCH(CH_3)-COOC_2H_5$, (b) $CH_3CO-\underset{\displaystyle C_2H_5}{\underset{|}{C}}(CH_3)-COOC_2H_5$

(c) $CH_3-CO-\underset{\displaystyle COCH_3}{\underset{|}{CH}}-COOC_2H_5$, (d) $CH_3-CO-\underset{\displaystyle CH_2CH=CH_2}{\underset{|}{CH}}-COOC_2H_5$

1028. Using acetoacetic ester, synthesize the following ketones: (a) 2-pentanone, (b) methyl isobutyl ketone, (c) allylacetone.

1029. Which of the following ketones: (a) methyl isopropyl ketone, (b) ethyl isobutyl ketone, (c) dipropyl ketone, can be obtained from acetoacetic ester? Write the reactions.

1030. Establish the structure of beta-keto ester, the ketone cleavage of which gives 3-pentanone. Obtain the starting beta-keto ester from propionic acid.

1031*. What compounds are formed by the following reactions?

$$CH_3COCH_2COOC_2H_5 \xrightarrow{CH_3CH_2ONa} \ldots \xrightarrow{I_2} \ldots \xrightarrow[(H^+),\ heat]{H_2O} \ldots$$

1032*. Write the reaction of ketone cleavage of methylene bis-oxaloacetic ester having the structure

$$\begin{array}{l} H_5C_2OOC-CH \quad CH_2 \quad CH-COOC_2H_5 \\ \qquad\qquad\quad | \qquad\quad | \\ H_5C_2OOC-CO \qquad CO-COOC_2H_5 \end{array}$$

1033. What compounds are formed by the action of concentrated solution of alkali on acetoacetic ester? Consider the mechanism of the reaction.

1034. Indicate what compounds are formed by the acid cleavage of the following beta-keto esters:

(a) $CH_3-CO-C(CH_3)_2-COOC_2H_5$, (b) $CH_3-CO-\underset{\displaystyle COCH_3}{\underset{|}{CH}}-COOC_2H_5$

(c) $CH_3-CH_2-CO-\underset{\displaystyle CH_2CH_3}{\underset{|}{C}}(CH_3)-COOC_2H_5$

(d) $CH_2=CH-CH_2-\underset{\displaystyle CO\\ \displaystyle CH_3}{\underset{|\\|}{CH}}-COOC_2H_5$

1035. Using acetoacetic ester, synthesize the following: (a) butyric acid, (b) dimethylacetic acid, (c) glutaric acid, (d) gamma-ketovaleric acid.

1036. Establish the structure of an alkyl acetoacetic ester, the acid cleavage of which gives 3-methylpentanoic acid. What product is formed in the ketone cleavage of this ester?

1037*. What compounds are formed from diacetyl succinate

$$\begin{array}{l} CH_3CO-CH-COOC_2H_5 \\ \qquad\quad | \\ CH_3CO-CH-COOC_2H_5 \end{array}$$

(a) by acid cleavage, (b) by ketone cleavage?

1038. Complete the following:

$$2CH_3CH_2COOC_2H_5 \xrightarrow[\text{heat}]{C_2H_5ONa} \ldots \xrightarrow[H^+]{H_2O} \ldots \xrightarrow[\text{alcohol}]{C_2H_5ONa}$$
$$\rightarrow \ldots \xrightarrow[\text{heat}]{CH_3CH_2Br} \ldots \xrightarrow[H^+]{H_2O} \ldots$$

D. Establishing the Structure of Organic Compounds by Their Properties

1039. What chemical conversion did acetoacetic ester undergo if the obtained product gives 3-methyl-2-pentanone on heating with a dilute acid? Write the reactions.

1040. Establish the structure of $C_5H_8O_3$ that is stable to heat, gives an oxime, does not react with ammoniacal silver oxide solution, and turns into *n*-valeric acid on reduction.

1041*. Establish the structure of beta-keto ester $C_8H_{14}O_3$ that gives diethyl ketone on heating with dilute acids. Obtain this ester by condensation process.

1042. A ketone having the molecular formula $C_{10}H_{20}O$ undergoes oxidation. The acid $C_8H_{16}O_2$ is isolated from the reaction products. The acid can also be synthesized by the action of *n*-hexyl bromide on sodium acetoacetic ester with subsequent decomposition of the obtained product by concentrated solution of an alkali on heating. Establish the structure of the starting ketone $C_{10}H_{20}O$.

1043. A substance having the formula $C_7H_{12}O_3$ does not react with soda solution, nor does it react with ferric chloride. When heated with concentrated alkali, it cleaves, and one of the reaction products is isobutyric acid. Establish the structure of the original compound.

CHAPTER FIFTEEN

OPTICAL ISOMERISM

A. Optical Isomerism of Compounds with One and Several Asymmetric Carbon Atoms

1044. What is 'optical activity' of substances? What is the measure of optical activity? How can it be determined experimentally?

1045. What property of a molecule of an organic substance does the optical isomerism depend on? What is 'asymmetric carbon atom'? Will the presence of an asymmetric carbon atom be sufficient to induce optical isomerism?

1046*. Give examples of optically active compounds: (a) containing an asymmetric nitrogen atom, (b) having no asymmetric atoms. Give examples of compounds having asymmetric carbon atoms but showing no optical activity.

1047. Determine the dependence of the number of optical isomers on the number of asymmetric centres. How many asymmetric carbon atoms does each of the following compounds contain?

(a) $CH_3—CH(CH_3)—CH(OH)—CH_3$

(b) $HOOC—CH(CH_3)—CHCl—COOH$

(c) $CH_2(OH)—CH(OH)—CHBr—C(=O)H$

(d) $CH_2(OH)—CH(OH)—CH(OH)—CH(OH)—CH(OH)—C(=O)H$

How many optical isomers correspond to each of them? How many racemic compounds are there among them?

1048. Write structural formulas of an alkyl halide and a carboxylic acid containing one asymmetric carbon atom, of a monohydric alcohol containing two different asymmetric carbon atoms. How many optical isomers correspond to each formula?

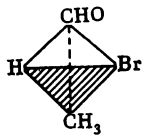
1049. Formulate Emil Fischer rule of making out projection formulas. Draw three-dimensional and projection for-

mulas for enantiomers of glyceraldehyde. What are the rules of using projection formulas?

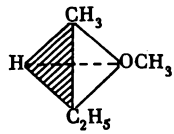
1050. Draw spatial and projection formulas of enantiomers of the following compounds:

(a) CH_3—CH(OH)—COOH, (b) CH_3—CHBr—CH_2OH

1051. Write Fischer projection formulas for the following compounds:



a



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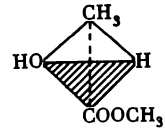

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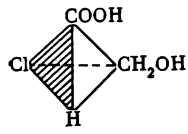

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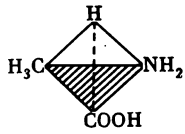

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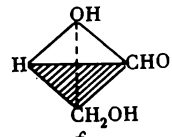

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Give three-dimensional formulas of enantiomers of each substance.

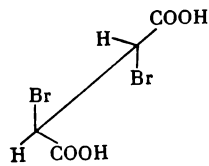
1052. Do enantiomers differ in their physical properties? Will geometric isomers differ in their physical constants? Give explanations using stereoisomers of *sec*-butyl alcohols and ethylenedicarboxylic acids as examples.

1053. Write projection formulas for all stereoisomers of α-chloro-α′-hydroxysuccinic acids. What stereoisomers are known as diastereoisomers? Do they differ in their properties?

1054. How many stereoisomers correspond to the formula of tartaric acid? Write projection formulas for all tartaric acids. Indicate which of them correspond to the optically active compounds. Which of the acids is known as mesotartaric acid?

1055. How can a *meso*-isomer be distinguished from a racemic compound?

1056*. Given below are perspective sawhorse formulas for stereoisomers of α,α′-dibromosuccinic acids:



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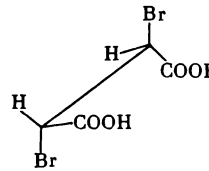

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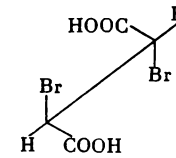


c

Give the corresponding Fischer formulas. Which of the acids are optically active compounds? Indicate the *erythro*- and *threo*-forms.

1057. Which of the compounds given below are enantiomers, diastereomers, identical substances? Are there *meso*-forms among them?

(a) C_2H_5, H—, —Br, Br—, —H, C_2H_5

(b) C_2H_5, H—, —Br, H—, —Br, C_2H_5

(c) CH_3, H—, —NH_2, H—, —NH_2, COOH

(d) COOH, H_2N—, —H, H_2N—, —H, CH_3

(e) COOH, H_2N—, —H, H—, —OH, C_3H_7

(f) COOH, H—, —NH_2, HO—, —H, C_3H_7

1058. How many optical isomers has the compound HOOC—CHCl—CHCl—CH_2OH? How many stereoisomers correspond to dicarboxylic acid that is formed during oxidation of this compound?

1059*. Which of the compounds given below can exist in the stereoisomeric forms, optically inactive because of the intramolecular compensation?

(a) $CH_2(OH)$—CHCl—CHCl—CH_2OH

(b) HOOC—CH(OH)—CH(OH)—$CONH_2$

(c) $HOCH_2$—CHI—CHI—CHI—CHI—CH_2OH

Write projection formulas of the corresponding *meso*-forms.

1060. Write a structural formula of a dihydric alcohol $C_4H_{10}O_2$, existing in the form of two optically active forms and one *meso*-form.

1061. How many stereoisomers has each of the following compounds: (a) $CH_3—CHBr—CHBr—CH_3$, (b) $CH_3—CHBr—CHBr—CH_2—CH_3$? Write projection formulas for enantiomers, *meso*-forms, and diastereoisomers.

1062*. How many optically active isomers, racemates, and *meso*-forms correspond to the compound?

$$HOCH_2—CH(OH)—CH(OH)—CH(OH)—CH_2OH$$

1063*. What is the geometry of the molecule of methylethylpropylamine? Can the compound be resolved into enantiomers? Develop your reasons.

1064*. What is the spatial structure of methylallylphenylbenzylammonium iodide? Is optical isomerism possible with this compound?

B. Stereometric Series. Relative and Absolute Configurations

1065. Using stereoisomers of glyceraldehydes as an example, explain what is understood by configuration of optically active compounds. What is configuration series? Define relative and absolute configurations.

1066*. To what stereochemical series (D- or L-) does each of the compounds given in Problem 1051, belong?

1067. State the general principle of establishing the configuration of optically active compounds by chemical methods. What is the configuration of glyceric acid that is formed: (a) by oxidation of D-glyceraldehyde, (b) by the action of nitrous acid on D-isocerine ($H_2N—CH_2—CH(OH)—COOH$)?

1068. What stereoisomers of tartaric acid are formed from D-glyceraldehyde, if it is acted upon with HCN with subsequent saponification and then oxidation of its reaction products?

1069*. What derivative of one of the tartaric acids is optically active, but becomes optically inactive because of methylation with diazomethane, or after hydrolysis?

1070. Will the configuration of D-*sec*-butylacetic acid change on esterification with ethyl alcohol?

C. Synthesis of Compounds with Asymmetric Carbon Atoms. Resolution of Racemates into Enantiomers

1071. Write reactions of acetaldehyde with hydrocyanic acid and subsequent hydrolysis of the obtained product. Will the end product be optically active? Develop your reasons.

1072. Explain why the reaction

$$CH_3CH_2CH_2COOH + Br_2 \longrightarrow CH_3CH_2CHBrCOOH + HBr$$

gives optically inactive alpha-bromobutyric acid.

1073. Write balanced equations for reactions and indicate which of them will give substances that can be resolved into optically active compounds: (a) reduction of levulinic acid to the corresponding hydroxy acid, (b) monochlorination of acetic acid, (c) chlorination of propionic acid to alpha-chloropropionic acid, (d) decomposition of ethylpropylmalonic acid with heating.

1074*. Consider the stereochemistry of reactions in which bromine is added to stereoisomers of 2-butene. What is the configuration of the formed compounds? (Mind the formation of intermediate bromonium ion).

1075*. What is the configuration of products of bromine addition: (a) to maleic acid, (b) to fumaric acid? Consider the mechanism of the reactions using sawhorse formulas.

1076*. Consider the stereochemistry of the reaction in which bromine is added to *cis*- and *trans*-crotonic acids. What is the configuration of the addition products?

1077. By what methods can racemates be resolved into enantiomers? Describe the principle of chemical resolution of racemic compounds. Explain, using resolution of racemic 2-aminobutane and racemic lactic acid, as examples.

1078. Explain why in the living body, compounds with asymmetric carbon atoms are formed in optically active

forms, and in laboratory in the form of racemic compounds.

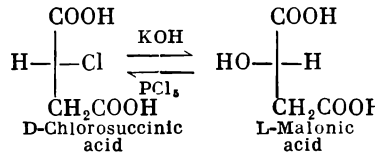
1079. What is asymmetric synthesis? Give examples of partial asymmetric synthesis.

D. Substitution Reactions at Asymmetric Carbon Atom. Walden Inversion

1080. Using hydrolysis of an optically active halogen derivative, $CH_3—CH_2CClCH_2CH_2CH_3$ (with CH_3 as a branch on the second carbon), as an example consider the stereochemistry of monomolecular nucleophilic substitution reactions. Explain the terms: inversion of configuration, retention of configuration, racemization.

1081. Using the reaction of optically active 2-bromooctane with potassium acetate as an example, consider the stereochemistry of bimolecular nucleophilic substitution reactions.

1082. What is known as Walden inversion? Give explanation using the following as an example:



1083*. The alcoholysis of which alkyl halide: (a) (+)-2-bromobutane or (b) (+)-3-bromo-2,3-dimethylpentane will cause deeper racemization? On what does this fact depend?

1084*. Explain the following: hydrolysis of optically active 2-chlorooctane occurs with inversion accompanied by its racemization by 30 per cent. A similar reaction with methylethylisohexylmethane chloride proceeds with partial inversion of configuration and loss of optical activity by 70 per cent.

1085. What is the configuration of methyl-*sec*-butyl ether obtained by the following methods: (a) by reaction of L-2-bromobutane with sodium methoxide, (b) by reaction of D-2-butanol with sodium metal and subsequent treatment of the obtained product with methyl bromide?

1086*. Will a compound obtained by hydrolysis of optically active *threo*-3-bromo-2-butanol with sodium hydroxide solution (S_N2) have optical activity?

1087*. Consider the mechanism of the reaction of L-2-butanol with $SOCl_2$: (a) in pyridine, (b) in an inert solvent. What is the configuration of the reaction products?

1088*. Accomplish the following conversion:

L-2-butanol ⟶ D-2-butanol

1089*. Obtain the following compounds: (a) D-2-chlorobutane from L-2-chlorobutane, (b) D-2-butanol from D-2-chlorobutane, (c) D-2-chlorobutane from L-2-bromobutane.

1090*. Consider the mechanism of nucleophilic substitution reactions of bromine in a weak alkaline medium of the following optically active compounds: (a) α-bromobutyric acid, (b) its methyl ester, (c) its amide. Indicate in which case the configuration is inverted and in which it is retained.

1091*. What is the stereochemical result of the following reactions: (a) of acetaldehyde with hydrocyanic acid, (b) of L-α-bromopropionic acid with AgOH, (c) of D-α-bromopropionic acid in a strongly alkaline medium?

1092. Hydrolysis of L-α-bromopropionic acid in a strongly alkaline medium occurs with full inversion. Hydrolysis in the presence of moist silver oxide occurs with retention of configurations. What conclusion concerning the mechanism of the reactions can be drawn?

1093*. What stereoisomer of tartaric acid is formed during hydrolysis of *erythro*-α,α′-dichlorosuccinic acid with moist silver oxide?

1094. Compare the behaviour of two optically active amyl alcohols, D-2-pentanol and L-2-methyl-1-butanol, in the following reactions: (a) reaction with HBr, (b) oxidation to carbonyl compounds, (c) esterification. Indicate in which case the asymmetric centre will be retained. What will the configuration of the newly formed products be like?

1095*. When an optically active methylethylacetic acid is heated, its optical activity slowly vanishes. Explain.

PART TWO

CYCLIC COMPOUNDS

CHAPTER SIXTEEN

ALICYCLIC COMPOUNDS

SATURATED ALICYCLIC COMPOUNDS

A. Isomerism. Nomenclature. Stereochemistry

1096. Write structural formulas of the following compounds: (a) 1,1-dimethylcyclopropane, (b) ethylcyclobutane, (c) pentamethylene, (d) cyclooctane, (e) 1,4-dimethylcyclohexane.

1097. Give structural formulas of all isomers of alicyclic hydrocarbons having the composition C_5H_{10}. Name them. Which of them will have geometric isomers? Optical isomers?

1098. Compare stereoisomerism of 2-butene and 1,3-dimethylcyclobutane. What is the cause of appearance of geometric isomers in each of these compounds?

1099. Write structural formulas of the following compounds: (a) *cis*-1,2-dibromocyclopropane, (b) *trans*-1,3-cyclopentanedicarboxylic acid, (c) *cis*-1,4-dimethylcyclohexane, (d) *trans*-1-methyl-2-ethylcyclopentane.

1100. Consider stereoisomerism of 1-methyl-2-ethylcyclopropane. How many compounds correspond to the given structural formula?

1101. Draw formulas of all stereoisomers of 1-methyl-3-ethylcyclobutane.

1102. Compare stereoisomerism of cyclopropane-1,2-dicarboxylic and tartaric acids.

1103. Write structural formulas of all homologues of cyclobutane having the composition C_6H_{12} that can exist in the form of *cis*- and *trans*-isomers. Which of them have optical isomers?

1104*. Draw a structural formula of a four-membered cyclic hydrocarbon having the composition C_7H_{14} to which correspond: (a) two spatial isomers, (b) four spatial isomers.

1105. Characterize the nature of the carbon-carbon bonds in three-, four-, five-, and six-membered rings.

1106. What is the essence of the Baeyer strain theory? What are modern concepts of the causes accounting for the stability of rings?

1107. Draw diagrams of formation of σ-, π- and bent or 'banana' carbon-carbon bond. How do their stabilities compare?

1108. Compare the concept of 'configuration' and 'conformation' and explain them using: (a) 2-butene, (b) lactic acid, (c) *n*-butane, and (d) 1,2-dimethylcyclohexane as examples.

1109. What configurations are possible for 1,2-dimethylcyclopentane? Name them.

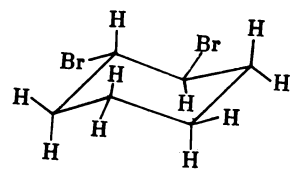
1110*. What configurations are possible for 1,2,3-trimethylcyclobutane? Name them.

1111*. In each pair of compounds: (a) methylcyclopropane and cyclobutane, (b) ethylcyclobutane and methylcyclopentane, (c) *cis-* and *trans*-1,3-dimethylcyclopentane, (d) *trans*-1,2-dimethylcyclobutane and cyclohexane, indicate a more stable isomer and explain its higher stability.

1112. Draw conformations of cyclohexane. Explain the higher stability of one of them.

1113. Characterize the spatial orientation of the C—H bonds in the chair conformation of cyclohexane. Draw axial and equatorial conformations of bromocyclohexane. Which of them is more stable?

1114*. Which of the names: (1) *cis*-1,2-dibromocyclohexane (*e*, *e*), (2) *cis*-1,2-dibromocyclohexane (*a*, *e*), (3) *trans*-1,2-dibromocyclohexane (*a*, *e*), (4) *trans*-1,2-dibromocyclohexane (*a*, *a*), (5) *trans*-1,2-dibromocyclohexane (*e*, *e*) correspond to the compound shown below?



1115*. What conformations are possible for *trans*-cyclohexane-1,2-dicarboxylic acid? Draw them. Which of them is more stable?

1116*. For what structural isomer of dimethylcyclohexane is the *cis*-configuration more stable than *trans*-configuration? Develop your reasons.

1117*. Draw stable conformations of *cis*- and *trans*-3-*tert*-butylcyclohexanol, bearing in mind that bulky substituents assume predominantly the equatorial position.

1118*. The dipole moment of *trans*-1,2-dibromocyclohexane is 2.11 D. What conclusion concerning the conformation of this compound can be made?

1119. In each pair of the compounds: (1) (*a*)-cyclohexanol and (*e*)-cyclohexanol, (2) *cis*- and *trans*-1,2-dimethylcyclohexane, (3) *cis*- and *trans*-1,3-dimethylcyclohexane, (4) *cis*- and *trans*-1,4-dimethylcyclohexane, indicate a more stable isomer and explain the cause of its higher stability.

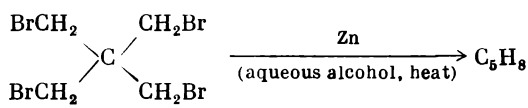
1120*. Hydrogenation of naphthalene in the presence of a platinum catalyst in acetic acid gives predominantly decalin (decahydronaphthalene). The product boils at 195°C (I). Hydrogenation of naphthalene in the gaseous phase on the MoS_3 catalyst gives decalin that boils at 185°C (II). Decalin (I) can be converted into decalin (II) in the presence of aluminium chloride. Explain.

B. Methods of Preparing Cycloalkanes and Their Derivatives

1121. Using the Wurtz reaction, obtain: (a) methylcyclopropane, (b) 1,2-dimethylcyclobutane, (c) methylcyclopentane. The yield of which product is higher?

1122. Suggest methods to synthesize: (a) cyclopropane from trimethylene glycol, (b) methylcyclobutane from the corresponding glycol.

1123*. What is the structure of the hydrocarbon C_5H_8 that is formed by the following reaction?



Name this hydrocarbon.

1124. Using malonic ester obtain the following: (a) 2-methylcyclopropanecarboxylic acid, (b) cyclobutanecarboxylic acid.

1125. Obtain cyclopentanone from adipic acid: (a) by pyrolysis in the presence of a catalyst, (b) via a calcium salt, (c) via ethyl ether.

1126. Write the process of preparing cyclopentane using the following starting substances: (a) 1,5-dibromopentane, (b) 1,5-pentanediol, (c) malonic ester, (d) ethyl adipate, (e) calcium adipate. Which of these methods is more rational?

1127*. Suggest a method to synthesize alpha-methylcyclopentanone from adipic acid.

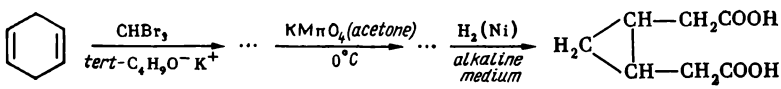
1128. Write the reaction of ester condensation of ethyl pimelate, $C_2H_5OOC—(CH_2)_5—COOC_2H_5$.

1129. Obtain alpha-hydroxycyclohexanone by acyloin condensation.

1130*. What products can be obtained by hydrolysis of compounds formed during heating ethyl adipate: (a) with 1 mole of sodium in alcohol, (b) with 4 moles of sodium in toluene in an atmosphere of nitrogen gas? Write the reactions.

1131*. What cyclopropane derivative can be obtained from tetramethylethylene by the action on it of chloroform and *tert*-potassium butylate? Write the reaction.

1132*. Cyclopropane-1,2-diacetic acid has been obtained from 1,4-cyclohexadiene as follows:

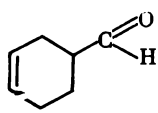


Write structural formulas of the intermediate compounds.

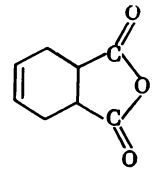
1133*. Fluorinated olefins are easy to dimerize. What cyclobutane derivative can be obtained from 1,1-dichloro-2,2-difluoroethylene?

1134. Hydrogenation of what aromatic compounds can give: (a) cyclohexane, (b) cyclohexane-1,4-dicarboxylic acid, (c) cyclohexane-1,3,5-triol? Specify the reaction conditions.

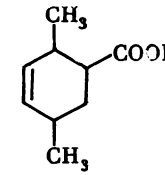
1135*. Using the reaction of diene synthesis obtain the following cyclohexane derivatives:



a



b



c

1136. Suggest a method for conversion of benzene into cyclopentane.

C. Properties of Alicyclic Compounds

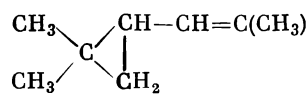
1137. Characterize the I-R and U-V spectra of cycloalkanes. Can *n*-hexane be distinguished from cyclohexane by their I-R spectra?

1138. Compare chemical properties of propylene and cyclopropane. Explain the similarity and differences.

1139. Write the reactions of cyclopropane: (a) with HBr, (b) with HI, (c) with H_2SO_4. Specify the conditions of the reactions and name the obtained products. Consider the mechanism of reaction (c).

1140. Suggest a method for purification of cyclopropane from traces of propylene. Write the reaction.

1141*. What compound is formed by oxidation of the substance



with aqueous $KMnO_4$ at room temperature?

1142. What conditions are required to realize the reaction of cyclopropane and cyclopentane with bromine? Write the reactions. Explain the differences.

1143. Using cyclohexane, hexane, and 1-hexene, compare the attitude of cycloparaffins, paraffins, and olefins to the action of aqueous solution of potassium permanganate in the cold and with heating.

1144. Indicate reactions by which the following isomers can be distinguished: 2-pentene, 1,2-dimethylcyclopropane, and cyclopentane.

1145. What reactions can be used to distinguish between ethylcyclobutane and cyclohexane.

1146. Write reactions of mononitration of cyclohexane, methylcyclopentane. Specify the conditions. What reaction can be used to distinguish between the obtained nitro compounds?

1147. Obtain (a) 1-propanol, and (b) 1,3-propanediol from cyclopropane.

1148. Write reactions of cyclohexanol: (a) with acetic acid in the presence of H_2SO_4, (b) with acetic anhydride, (c) with phosphorus pentachloride. What compounds are formed by dehydration of cyclohexanol? by its oxidation?

1149*. What conformation of *cis*-2-methylcyclohexanol will easier enter the following reactions: (a) esterification with acetic acid, (b) oxidation to ketone? What conformation of *cis*-2-methylcyclohexanol acetate is easier to hydrolyze?

1150. Write the reactions of cyclohexanol with sodium bisulphite, HCN, C_2H_5MgBr, and NH_2OH. Consider the mechanism of the latter two reactions.

1151*. Compare the reactivity of cyclobutanol and cyclopentanone in reactions with hydrocyanic acid. Give explanations.

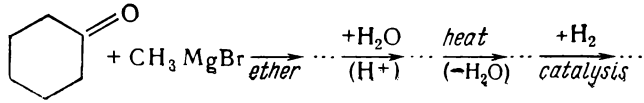
1152*. Explain why cyclohexanone is easier to enter nucleophilic addition reactions than cyclopentanone. Prove your answer by considering angle and conformational strains in the starting and end products.

1153. Suggest several methods to convert cyclopentanone into cyclopentane.

1154. Obtain epsilon-aminocaproic acid from cyclohexanone using the Beckmann rearrangement.

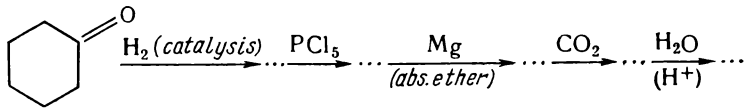
1155*. Indicate a chemical method for separation of cyclohexanone from cyclohexanol.

1156. Fill in the missing structural formulas of the intermediate and end products into the following:



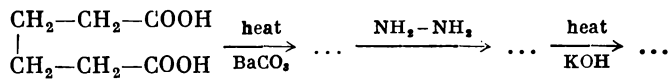
1157*. What compound is obtained by the reaction of cyclohexanone with diazomethane?

1158. Complete the following:



Draw the most stable conformation of the end product.

1159. What compounds are formed by the following conversions:



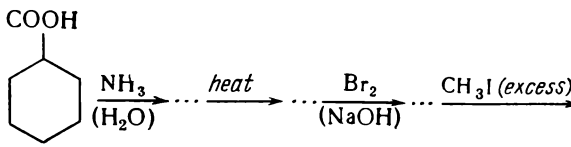
1160. Compare the attitude of nitrocyclohexane and 1-nitro-1-methylcyclopentane toward aqueous solutions of alkalis. Write the reactions. Explain.

1161. Suggest a chemical method of separation of nitrocyclohexane from cyclohexane.

1162. What products are formed by the reaction of cyclohexylamine: (a) with HCl, (b) with nitrous acid, (c) with methyl iodide, (d) with acetic anhydride?

1163. Write structural formulas of the following naphthenic acids: (a) cyclopentanecarboxylic acid, (b) cyclopentylacetic acid, (c) 4-methylcyclohexanecarboxylic acid, (d) 2,2,6-trimethylcyclohexanecarboxylic acid. Indicate a chemical method of their separation from hydrocarbons.

1164. Fill in structural formulas of the intermediate and end products in the following:



1165*. Synthesize alpha-isopropylcyclopentanone from alpha-carbethoxycyclopentanone.

D. Ring Isomerization

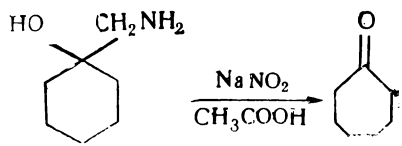
1166*. Write the reversible isomerization of cyclohexane in the presence of aluminium chloride. How will cycloheptane behave in these conditions? What conclusion concerning relative stability of rings can be made from these conversions?

1167*. What compound will be obtained by the action of alkali on alpha-chlorocyclohexanone in the absence of water? in an aqueous solution?

1168*. Write the reaction of cyclobutylamine with nitrous acid. Consider its mechanism.

1169*. The reaction of nitrous acid with cyclopropylaminomethane gives a mixture of cyclopropylcarbinol and cyclobutanol. Why?

1170*. Cycloheptanone is obtained by the action of nitrous acid on 1-aminomethylcyclohexanol:



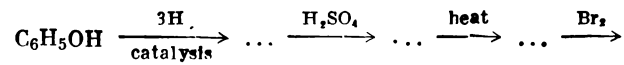
The yield is 57-65 per cent. Explain the mechanism of the conversion.

UNSATURATED ALICYCLIC COMPOUNDS

1171. Suggest a method for preparing cyclopentene: (a) from cyclopentane, (b) from adipic acid.

1172. Obtain cyclopentadiene from cyclopentane. Characterize the properties of this unsaturated compound.

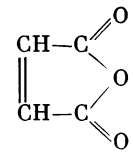
1173. What compound will be obtained by the following conversions?

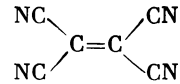


Draw the most stable conformation of the end product.

1174. Complete the following:

(a) $CH_2=CH-CH=CH_2+CH_2=CH-CHO \xrightarrow{100°C} \ldots$

(b) $CH_2=CH-CH=CH_2+$  $\xrightarrow[\text{benzene}]{100°C} \ldots$

(c) $CH_2=CH-CH=CH_2+$  $\xrightarrow[\text{tetrahydrofuran}]{20\ °C} \ldots$

Name the reaction products.

1175. What cyclic hydrocarbon is formed by heating trimethylcyclopropylammonium hydroxide? Characterize its properties.

1176. What compounds are formed by the action of $KMnO_4$ solution on cyclopentene at room temperature? with heating? Write the reaction of cyclopentene ozonolysis.

1177. Write the reaction of ozonolysis of cyclobutene, 1-methyl-2-ethylcyclopentene, and 3-propylcyclohexene.

1178. Compare the properties of hexane, cyclohexane, and cyclohexene. Explain the differences.

1179*. Write the reaction of hydration of 1,2-dimethylcyclohexene in the presence of acids. Consider the reaction mechanism and spatial structure of the formed products.

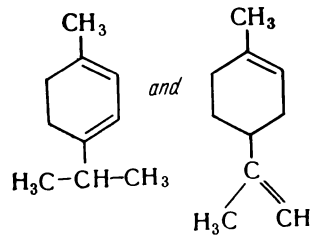
1180*. What compound is formed by the action of bromine on cyclopentene with heating the obtained product with excess CH_3COOK in acetic acid medium? Write the reactions.

1181*. Write the reactions of cyclopentadiene with: (a) bromine (1 mole), (b) acetaldehyde, (c) diethylketone, (d) maleic anhydride, (e) acrolein, (f) acetylenecarboxylic acid.

1182*. What compounds are formed by the action of cyclopentadiene on potassium? on CH_3MgBr? What accounts for the activity of the hydrogen atom of the methylene group of cyclopentadiene?

1183. Indicate the differences in the properties of the

following isomers:



Write the reactions.

1184*. Give examples of cyclic compounds with a triple bond in the ring. What accounts for the impossibility of existence of lower rings with triple bonds?

E. Establishing the Structure of Organic Compounds by Their Properties

1185*. There are two isomers having the composition C_5H_{10}, (I) and (II). Bromine reacts with (I) to give C_5H_9Br, and the compound (II) gives $C_5H_{10}Br_2$. The compound (I) is oxidized to give the acid $C_5H_8O_4$, whereas the compound (II) gives a mixture of acetic and propionic acids. Write structural formulas of the compounds (I) and (II).

1186*. Write a structural formula of a hydrocarbon having the composition C_6H_{12} which: (1) does not decolourize aqueous solution of $KMnO_4$ at room temperature, (2) reacts with HI with formation of $C_6H_{13}I$, (3) is hydrogenated to give the only product, methyldiethylmethane.

1187. Establish the structure of the hydrocarbon C_6H_{10} by the following: (1) the I-R spectrum has an absorption band at 1640 cm^{-1}, (2) oxidation of the compound gives adipic acid.

1188*. Establish the structure of the hydrocarbon C_9H_{16} that decolourizes bromine water and is oxidized to give γ-ethylpimelic acid.

1189*. Draw a formula of a cyclic hydrocarbon having the composition C_6H_{12}, which is stable to bromine water and hydrogen iodide, has the *trans*-configuration, and cannot be resolved into optical antipodes.

1190. Establish the structure of a compound having the

composition $C_6H_{12}O$, which reacts with acetic anhydride to give $C_8H_{14}O_2$, and is oxidized to give adipic acid. Draw possible conformations of this compound. Which of them is the most stable?

1191*. Determine the structure of a cyclic compound having the composition $C_5H_8O_2$ that easily reacts with soda,

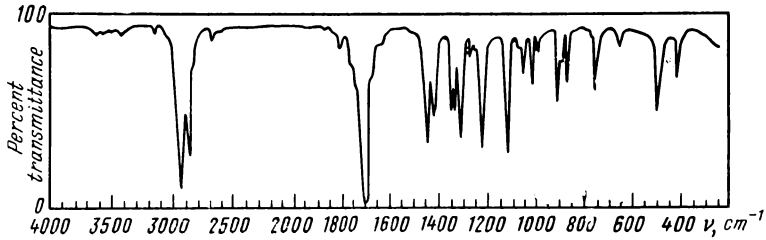


Fig. 32. I-R spectrum of $C_6H_{10}O$

readily adds bromine, and has the *trans*-configuration. Is optical isomerism possible with this compound?

1192*. Figure 32 shows the I-R spectrum of the compound $C_6H_{10}O$ (liquid film). Establish the structure of this compound: it is oxidized to give adipic acid.

1193*. Write a structural formula of a compound having the composition $C_6H_{10}O$ that reacts to carbonyl group and is oxidized into a mixture of α- and β-methylglutaric acids.

1194*. What is the structure of an acid (a constituent part of fats) that decolourizes bromine water and is ozonolyzed to give 9,11-diketo-nonane-decanoic acid?

1195*. Establish a structural formula of a cyclic compound having the composition $C_5H_6O_4$ that reacts with sodium bicarbonate to give the salt $C_5H_4O_4Na_2$. The compound $C_5H_6O_4$ does not form anhydride, is optically inactive, but can be separated into the optical antipodes. What is the configuration of the compound $C_5H_6O_4$?

1196*. Draw a formula of a cyclobutanedicarboxylic acid derivative that is optically active, but turns optically inactive on methylation with diazomethane and also on hydrolysis.

1197*. What conclusion concerning the structure of C_8H_{16} can be made, if the NMR spectrum of the compound has a single, very sharp line (δ 1.5 ppm, relative to TMS)?

CHAPTER SEVENTEEN

AROMATIC COMPOUNDS

A. Benzene Structure. Criterion of Aromaticity. Nonbenzoid Aromatic Compounds

1198. What properties of benzene and its derivatives are classified as 'aromatic'?

1199. Write a formula of benzene suggested by F. A. Kekulé. What are advantages and disadvantages of this formula?

1200. Give facts that prove equivalence of all the six carbon-carbon bonds in the benzene ring, and also of all six hydrogen atoms of benzene.

1201. What products are formed by ozonolysis of: (a) benzene, (b) toluene, (c) 1,2,4-trimethylbenzene?

1202. Write the Kekulé-Thiele formula of benzene. Describe the importance of the theory of residual valencies for the explanation of benzene properties. Does the Thiele theory explain the properties of 1,3,5,7-cyclooctatetraene?

1203. What compound is formed by exposure of a mixture of benzene and chlorine to sunlight? Characterize the addition reactions of benzene.

1204. What are the modern concepts of benzene structure? On what experimental data are they based?

1205. Define the concept of conjugation energy. What is the conjugation energy of benzene? Indicate experimental methods of its determination.

1206. Give explanations to 'aromatic' properties of benzene in the light of modern concepts of its structure.

1207. Characterize the structure of organic compounds that show aromatic properties. Formulate the Hückel rule. Give examples of aromatic carbo- and heterocyclic compounds.

1208*. Which of the following compounds: (a) 1,3-cyclohexadiene, (b) 1,3-cyclobutadiene, (c) pyridine, (d) borazole, (e) cyclopentadiene, (f) thiophene, (g) furan have aromatic properties?

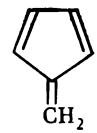
1209. Characterize the structure and properties of 1,3,5,7-cyclooctatetraene. Explain why this compound has no aromatic properties.

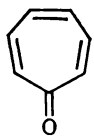
1210. Name carbocyclic aromatic systems obeying the Hückel rule if (a) $n = 0$, (b) $n = 1$, (c) $n = 2$.

1211*. Write formulas of the following hydrocarbons: (a) cyclopropene, (b) 1,3-cyclopentadiene, (c) 1,3,5-cycloheptatriene, (d) 1,3,5,7-cyclooctatetraene, (e) 1,3,5,7-cyclononanetetraene. What ions corresponding to these compounds will have aromatic properties?

1212*. Write the reactions of preparing the following compounds containing aromatic ions: (a) cyclopentadienylpotassium, (b) cycloheptatrienylium bromide.

1213. What compound is formed by the reaction of cyclopentadienylpotassium with $FeCl_2$? Characterize its structure and properties.

1214*. Explain why compounds like fulvene 

and tropone 

have significant dipole moments.

1215*. What is the structure of the compound C_7H_7Br that is formed by heating the product of bromine addition (1 mole) to cycloheptatriene?

1216*. Explain why tropone reacts with acids to give salts?

1217*. Tropolone has acid properties ($pK_a = 6.7$). Explain.

1218*. Draw a structure of an azulene molecule. In what direction does the electrophilic substitution reaction predominantly proceed in this compound?

1219*. Explain the following: azulene is extracted from an organic solvent by a 60 per cent sulphuric acid, its blue colour vanishing in this process. As the sulphuric acid solution is diluted with water, the starting hydrocarbon is liberated.

B. Electrophilic Substitution Reactions. Substitution Rules

1220. What reactions are known as electrophilic substitution reactions? Write the reaction of electrophilic substitution for benzene in the general form. Give examples.

1221. What is the mechanism of the reaction of an electrophilic reagent (e.g. $\overset{+}{N}O_2$) with a benzene molecule? What experimental facts prove it?

1222. Draw the energy diagram of the electrophilic substitution reaction in benzene. What points of the curve correspond to the intermediate compound? transition states?

1223. What is the difference between the transition state and an intermediate product? between σ- and π-complexes?

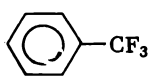
1224. Consider the structure of σ-complex that is formed by the reaction of benzene with an electrophilic reagent (E^+). What are the valence states of the carbon atoms? How is the positive charge distributed?

1225*. Compare the mechanism of electrophilic addition to alkenes with that of electrophilic substitution in an aromatic series, using the reactions of ethylene and benzene with bromine as examples. At what stage do the differences show and why?

1226. Using ethylbenzene and nitrobenzene as examples, characterize the effect of electron-donating and -accepting substituents on the direction and rate of the reactions of electrophilic substitution in the benzene series. Formulate the substitution rules.

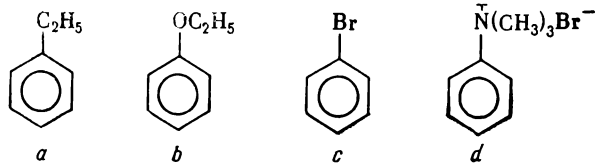
1227. What three competing reactions are possible in mononitration of toluene? In what direction will the substitution reaction predominantly occur?

1228. Compare stabilities of intermediate compounds (σ-complexes) that are formed in *ortho*-, *meta*-, and *para*-substitution of bromine for hydrogen atoms in methoxybenzene (in the presence of a catalyst). Determine the directing effect of the methoxy group.

1229. Explain why in nitration of trifluorophenylmethane  the yield of the *meta*-isomer is 100 per cent.

1230. Explain why the groups $-NO_2$ and $-CHO$ should be *meta*-directors and have deactivating properties.

1231. Characterize and explain the effect of substituents on the direction and rate of electrophilic substitution in the following compounds:



1232. Write the reactions of mononitration of the following compounds: (a) phenol, (b) benzenesulphonic acid, (c) isopropylbenzene, (d) chlorobenzene. For what compound will the rate of substitution be higher and why?

1233. Explain the formation of what products should be expected in monosulphonation of the following compounds: (a) toluene, (b) nitrobenzene, (c) benzoic acid, (d) bromobenzene? What compound is the easiest to sulphonate?

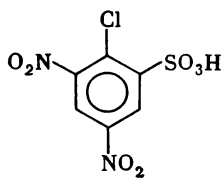
1234. Arrange the following compounds in the order of their increasing rate of bromination (in the presence of a catalyst): (a) benzene, (b) phenol, (c) benzoic acid, (d) propylbenzene. Develop your reasons.

1235*. What is the partial rate factor? Give examples of compounds for which: (a) f_o, f_m and f_p are greater than 1, but f_o and f_p are greater than f_m; (b) f_o, f_p are greater than 1; f_m is less than 1, (c) f_o, f_p and f_m are less than 1, but f_m is greater than f_p and f_o.

1236. In what order should substituents be introduced during preparation of the following compounds from benzene: (a) *m*-nitrochlorobenzene, (b) *m*-bromobenzene-sulphonic acid, (c) 2,4-dinitrotoluene? Write the reactions.

1237. Indicate methods for preparing all isomers of nitrobromobenzenes from benzene.

1238. Suggest the most rational method for preparing the following compounds from benzene:



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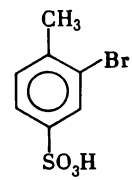

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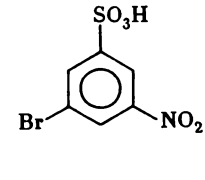
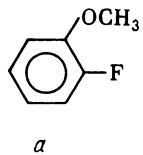


c

1239. Determine the position in which bromination of the following compounds will predominantly occur:



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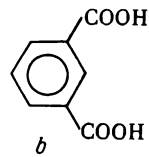

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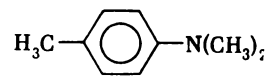

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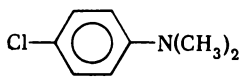

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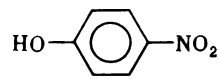


e

Indicate compounds with concerted orientation of the substituents.

1240*. During nitration of toluene, benzyl bromide, benzyl chloride and benzyl fluoride, in addition to the main reaction products, viz., *ortho-* and *para*-nitro derivatives, obtained also are *meta*-nitro derivatives in the quantities 3, 7, 14, and 18 per cent, respectively. Explain the results.

1241*. The yields of *meta*-isomer in nitration of nitrobenzene, phenylnitromethane, and 1-nitro-2-phenylethane are 93, 67, and 13 per cent respectively. Why?

1242. What factors affect the quantitative ratio of *ortho-* and *para*-isomers in electrophilic substitution in the benzene nucleus? Give examples.

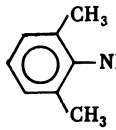
1243*. Explain why the alkylation of toluene with methyl bromide, isopropyl bromide, and *tert*-butyl bromide, alongside with the main reaction products (*ortho-* and *para-*

dialkylbenzenes), gives also *meta*-isomers in quantities 9.9, 17.6, and 32.7 per cent respectively.

1244*. Why does the quantity of *ortho*-isomer in chlorination of toluene, isopropylbenzene and *tert*-butylbenzene make 60, 22 and 0 per cent respectively?

1245*. Why are *ortho*- and *para*-isomers formed in the ratio of 7 : 9 in chlorination of chlorobenzene and 1 : 2 in bromination of chlorobenzene?

1246*. Explain why chlorination of 2,6-dimethylacetylide



is 15 times slower than chlorination of benzene, and 2,6-dimethyl-3-chloroacetylide is predominantly formed.

1247. Does benzene enter the nucleophilic substitution reaction? In the presence of what substituents can the hydrogen of the benzene ring be replaced by the nucleophilic reagent?

1248. What compounds are expected as a result of heating nitrobenzene with solid sodium hydroxide? Explain the mechanism of the reaction. What director is the nitro group in the given reaction?

CHAPTER EIGHTEEN

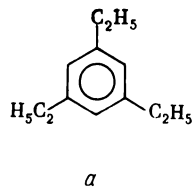
AROMATIC HYDROCARBONS

A. Isomerism. Nomenclature

1249. Write structural formulas for all isomeric aromatic hydrocarbons having the composition C_8H_{10} and C_9H_{12}. Name them according to the IUPAC system.

1250. Name the following univalent residues of aromatic hydrocarbons (aryls): C_6H_5-, $C_6H_5CH_2-$, *o*-$CH_3C_6H_4-$, *m*-$CH_3C_6H_4-$, and *p*-$CH_3C_6H_4-$.

1251. Name the following compounds:



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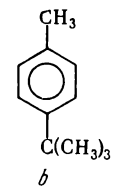

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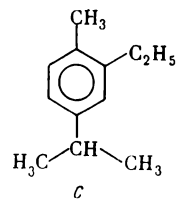

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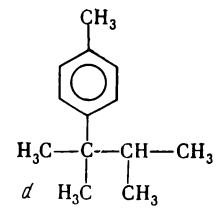

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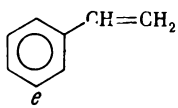

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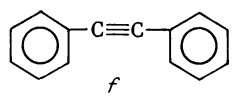

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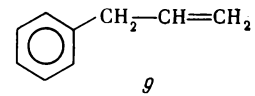


g

1252. Draw structural formulas of the following compounds: (a) *o*-xylene, (b) cumene, (c) *p*-cymene, (d) mesitylene, (e) styrene.

1253. Derive structural formulas for all the trisubstituted homologues of benzene having the composition $C_{10}H_{14}$. Name them.

B. Methods of Preparing

1254. Indicate commercial methods of preparing benzene and toluene.

1255. What is the essence of aromatization of petroleum? Under what conditions is it accomplished?

1256. Obtain benzene, and also toluene according to the following:

$$\text{alkane} \longrightarrow \text{cycloalkane} \longrightarrow \text{aromatic hydrocarbon}$$

What conditions are required to accomplish these conversions?

1257*. What aromatic hydrocarbons are formed by dehydrocyclization of octane?

1258*. What compound will be formed if a mixture of cyclohexane and cyclopentane is heated to 300°C in the presence of platinum?

1259. What aromatic hydrocarbons can be obtained: (a) by passing vapour of 1,2-dimethylcyclohexane over sulphur at 230-250°C, (b) by heating 1,3,5-trimethylcyclohexane in the presence of palladium deposited on activated carbon? Write the reactions.

1260*. Specify the conditions for aromatization of acetylene hydrocarbons. What aromatic hydrocarbon can be obtained from (a) 2-butyne, (b) 3-hexyne, (c) 1-hexyne?

1261*. What aromatic hydrocarbons are expected from heating the following ketones in the presence of sulphuric acid: (a) acetone, (b) acetophenone, $C_6H_5COCH_3$, (c) cyclohexanone

1262. Obtain benzene from the following compounds: (a) cyclohexane, (b) benzoic acid, (c) benzenesulphonic acid, (d) phenol?

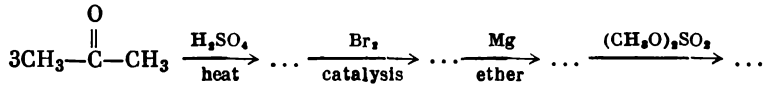
1263. What hydrocarbons can be formed by heating a mixture of bromobenzene and butyl bromide with sodium metal? Name the main product of this reaction.

1264. Using the Wurtz-Fittig synthesis obtain *p*-xylene from *p*-bromotoluene. Consider the mechanism of the reaction. What side products are formed in the reaction?

1265. Suggest a method for preparing *n*-butylbenzene from bromobenzene, *n*-butyl alcohol and inorganic reagents. What hydrocarbons are formed as side products?

1266. What compounds can be obtained from benzylmagnesium chloride by the action on it of (a) water, (b) ethyl alcohol, (c) benzyl chloride, (d) ethyl bromide, (e) diethyl sulphate?

1267*. What hydrocarbon is formed by the following conversions?



1268. Write the reaction for preparing ethylbenzene from benzene and ethyl chloride by the Friedel-Crafts method. Consider its mechanism. Why is it impossible to obtain ethyl benzene by the same method from ethane and chlorobenzene?

1269. What is the role of aluminium chloride in the alkylation of aromatic hydrocarbons by the Friedel-Crafts method? What other catalysts can be used in this reaction? Consider the mechanism of the reaction between toluene and isopropyl bromide in the presence of boron trifluoride.

1270. Characterize the Friedel-Crafts alkylation of aromatic hydrocarbons. What limits the use of this reaction? Give examples of aromatic compounds of various classes that do not enter the Friedel-Crafts reaction.

1271*. Why is isopropylbenzene the main product in the alkylation of benzene with propyl bromide or isopropyl bromide in the presence of aluminium chloride?

1272*. What hydrocarbon should be expected in the reaction of benzene with 1-chloro-2-methylbutane in the presence of aluminium chloride?

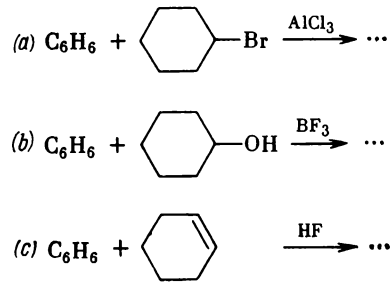
1273*. Why does the reactivity of alkyl halides, having the same radical, decrease in the Friedel-Crafts reaction from alkyl fluoride to alkyl iodide?

1274. Arrange alkyl halides: (a) ethyl bromide, (b) *tert*-butyl bromide, (c) allyl bromide, (d) 2-bromobutane, in the order of their increasing activity in the Friedel-Crafts reaction. Develop your reasons.

1275*. Treatment of hexamethylbenzene with methyl chloride in the presence of aluminium chloride gives a salt that is stable in an aqueous solution. Establish the structure of the salt. How can its stability be explained?

1276. Use the reaction of preparing isopropylbenzene from benzene to illustrate the action of various alkylating agents in the Friedel-Crafts reaction.

1277*. Write the following reactions:



Consider the mechanism of each reaction.

1278*. What hydrocarbon is predominantly formed by treating a mixture of xylenes with two moles of methyl chloride in the presence of aluminium chloride?

1279*. Suggest a method for preparing: (a) styrene, (b) α-methylstyrene from benzene.

1280. Which of the following aromatic hydrocarbons: (a) ethylbenzene, (b) isopropylbenzene, (c) *tert*-butylbenzene, (d) 2,2-dimethyl-5-phenylpentane, (e) propylbenzene can be obtained from benzene by the Wurtz-Fittig reaction and which by the Friedel-Crafts reaction? Which of them can be formed by both reactions?

1281. Obtain butylbenzene: (a) from benzene, (b) from bromobenzene, (c) from phenyl propyl ketone.

1282. Suggest a method for preparing benzene from methane.

1283. By what conversions can benzene be obtained from pimelic acid?

C. Properties

1284. By what absorption bands do the I-R spectra of aromatic hydrocarbons correlate with their structure?

1285. Consider the I-R spectrum of ethylbenzene (liquid film, Fig. 33). Indicate what frequencies correspond to the oscillations of the aromatic ring and its C—H bonds.

1286. Characterize absorption of benzene, toluene, and styrene in the U-V region.

1287. Consider the NMR spectrum of *p*-xylene (Fig. 34) and identify resonance signals of protons of the methyl groups and the benzene ring. Correlate the number of equivalent protons to the integral curve.

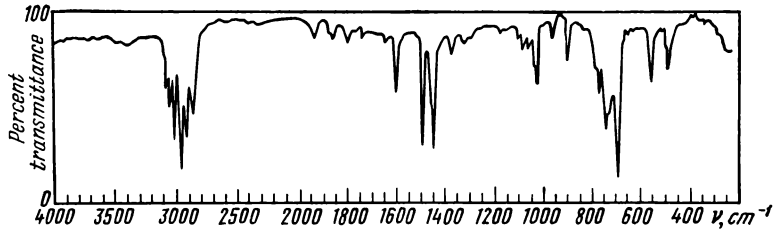


Fig. 33. I-R spectrum of ethylbenzene

1288. Using the modern concept of benzene structure, explain why benzene is characterized by electrophilic substitution reactions and not by addition reactions.

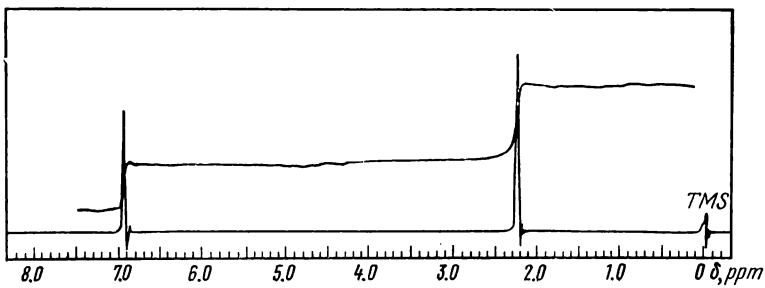


Fig. 34. NMR spectrum of *p*-xylene

1289. Write most important reactions of electrophilic substitution using ethylbenzene as an example.

1290. Write structural formulas of intermediate and final products in the following conversions:

$$C_6H_6 \xrightarrow[AlCl_3]{n\text{-}C_3H_7Br} \cdots \xrightarrow[H_2SO_4]{HNO_3} \cdots \xrightarrow[FeCl_3]{Cl_2} \cdots \xrightarrow[H_2O,\ heat]{KMnO_4} \cdots$$

1291*. What compounds are formed by the following conversions?

$$C_6H_6 \xrightarrow[HF]{(CH_3)_2C=CH_2} \ldots \xrightarrow[AlCl_3]{CH_3CH_2Br} \ldots \xrightarrow[H_2SO_4]{K_2Cr_2O_7} \ldots$$

1292. What characterizes the addition reactions of benzene? Why cannot the catalytic hydrogenation of benzene be used for preparing cyclohexene or cyclohexadiene?

1293. What compound is formed by heating 1,3,5-trimethylbenzene and hydrogen in the presence of finely divided nickel?

1294. Suggest a method to synthesize the following compounds from benzene: (a) propylcyclohexane, (b) 1,4-dimethylcyclohexane.

1295. Write the reaction of benzene with chlorine: (a) with exposure to sunlight, (b) in the presence of ferric chloride as a catalyst, the reactants being taken in the equimolecular ratio, and also with chlorine excess. What are the mechanisms of the reactions?

1296. What compounds are formed by ozonolysis of *m*-xylene? sym-trimethylbenzene?

1297. Explain how styrene will react with the following reagents: (a) bromine water, (b) aqueous solution of $KMnO_4$ in the cold, (c) aqueous solution of $KMnO_4$ on heating, (d) hydrogen bromide, (e) hydrogen in the presence of platinum in the cold.

1298. What is the structure of the products obtained by energetic oxidation of the following compounds: (a) butylbenzene, (b) *m*-diethylbenzene, (c) allylbenzene?

1299. Write the reaction of benzene oxidation to maleic anhydride. Specify the reaction conditions.

1300. Write the reactions of phenylacetylene with the following substances: (a) bromine water, (b) dilute sulphuric acid, in the presence of $HgSO_4$, (c) $Cu(NH_3)_2OH$, (d) $K_2Cr_2O_7 + H_2SO_4$ with heating.

1301*. What compound will be obtained by the action of potassium metal on toluene (in the presence of Na_2O) and subsequent treatment of the reaction product with carbon dioxide?

D. Establishing the Structure of Organic Compounds by Their Properties

1302. Write a structural formula of a hydrocarbon having the composition C_9H_{12}, the oxidation of which gives benzene-1,3,5-tricarboxylic acid.

1303. Oxidation of $C_{10}H_{14}$ with chromic-sulphuric acid on heating gives terephthalic acid, and oxidation in milder

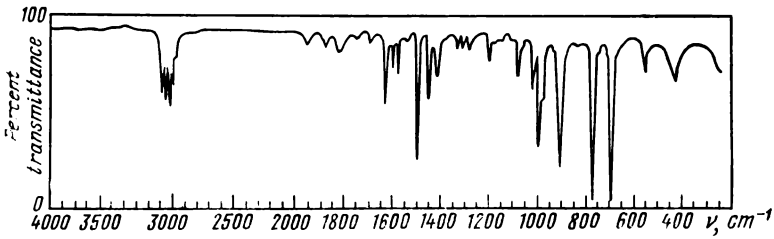


Fig. 35. I-R spectrum of C_8H_8

conditions gives *p*-toluic acid. What conclusion concerning the structure of this compound can be drawn?

1304. Establish the structure of an aromatic hydrocarbon having the composition C_9H_{12} monohalogenation of which gives only one compound.

1305*. Write possible structural formulas of aromatic hydrocarbons the ozonolysis of which gives a mixture of glyoxal, methylglyoxal, and dimethylglyoxal.

1306. Write a structural formula of the hydrocarbon C_8H_8 that decolourizes bromine water, easily polymerizes, and is oxidized into benzoic acid. Compare the structure of this hydrocarbon with its I-R spectrum (liquid film, Fig. 35).

1307. Determine the structure of an aromatic hydrocarbon having the composition $C_{10}H_{14}$ that contains an asymmetric carbon atom and is oxidized into benzoic acid. Obtain this hydrocarbon from benzene.

1308*. Determine the structure of a compound having the composition $C_{10}H_{10}$ that has the following properties: (a) it does not give precipitate with an ammoniacal solution of cuprous oxide, (b) when heated with dilute sulphuric acid in the presence of $HgSO_4$, it gives $C_{10}H_{12}O$ that reacts with hydroxylamine, (c) it is oxidized into isophthalic acid.

1309*. The hydrocarbon C_9H_{10}, the U-V spectrum of which is given in Fig. 36 (petroleum ether), is oxidized with potas-

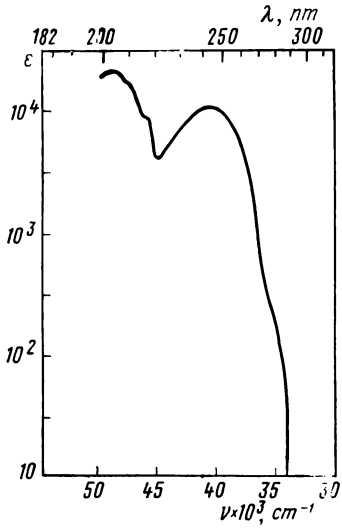
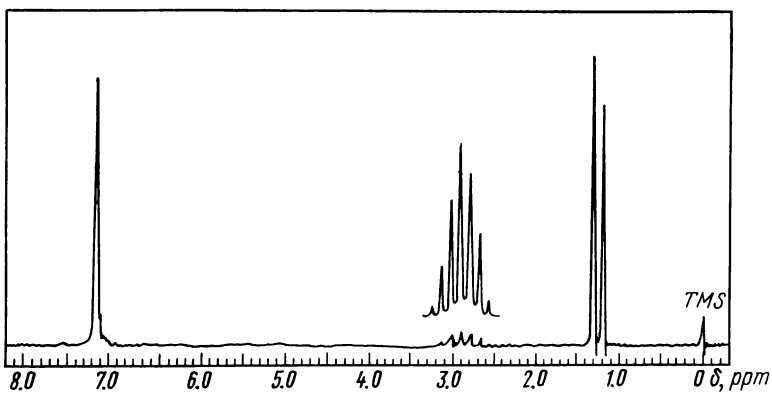


Fig. 36. U-V spectrum of C_9H_{10}

Fig. 37. NMR spectrum of C_9H_{12}



sium dichromate in an acid medium to give benzoic acid. Is it possible to establish the structure of C_9H_{10} from these data?

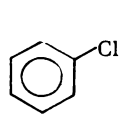
1310*. Establish the structure of the aromatic hydrocarbon C_9H_{12} by its NMR spectrum (Fig. 37).

CHAPTER NINETEEN

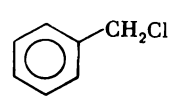
HALOGEN DERIVATIVES OF AROMATIC HYDROCARBONS

A. Isomerism. Nomenclature

1311. Name the following compounds:



a



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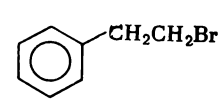

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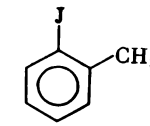

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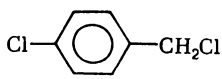

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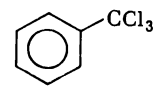

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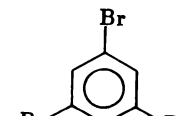


g

1312. Write structural formulas of the following compounds: (a) *p*-chlorotoluene, (b) benzylidene chloride, (c) unsym-tribromobenzene, (d) ω-iodopropylbenzene.

1313. Write structural formulas of isomeric halogen-substituted aromatic compounds having the formula C_7H_7Cl and name them.

1314. Write structural formulas of all isomers of monobromo-derivatives of propylbenzene. Name them.

B. Methods of Preparing

1315. Write the reaction of benzene bromination in the presence of iron. Consider the mechanism of the reaction. What other catalysts can be used to introduce a halogen into the nucleus?

1316. Draw the structure of σ-complexes that are formed by bromination of toluene, and also mesitylene, in the presence of ferric bromide. Explain which of the hydrocarbons is easier to be brominated.

1317*. What experimental dataprove the electrophilic character of the halogenation into the benzene ring in the presence of catalysts? Consider the mechanism of benzene iodination in the presence of silver sulphate.

1318. Write and explain the reaction of chlorination (in the presence of catalysts) of the following compounds: (a) ethylbenzene, (b) mesitylene, (c) nitrobenzene, (d) phenol. Which of these compounds is the easiest to be chlorinated?

1319. Bearing in mind electronic and spatial factors interpret the following experimental data concerning the proportion of isomeric products of monochlorination of toluene and *tert*-butylbenzene:

	Position		
	ortho-	*meta-*	*para-*
Toluene, per cent	59.8	0.5	39.7
tert-Butylbenzene, per cent	21.8	2.2	76.0

1320. In what conditions can the aromatic nucleus be iodinated directly?

1321. What product is formed by chlorination of 1,3-bis-(trichloromethyl) benzene in the presence of a catalyst?

1322*. What is the main product of benzene tetrachlorination?

1323. Write the reactions of preparing (a) iodobenzene, (b) fluorobenzene from aniline.

1324*. Suggest a method of preparing *m*-bromotoluene from *p*-toluidine.

1325. What compounds are formed by chlorination of toluene in the light without catalysts? Compare the mechanism of toluene chlorination into the side chain and in the nucleus.

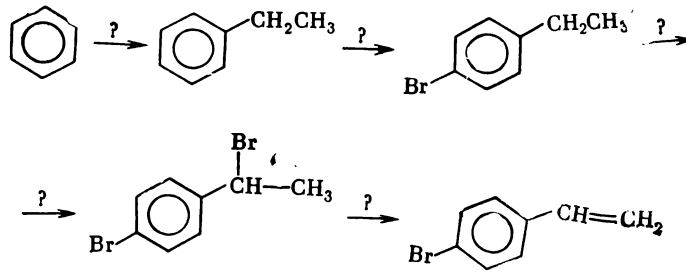
1326. Write the reaction of propylbenzene chlorination into the side chain and consider its mechanism.

1327. Compare the mechanism of methane and toluene chlorination in the light in the absence of catalysts. How can the easier chlorination of toluene be explained?

1328. Write structural formulas of all monobromo-derivatives of ethylbenzene. Which of these compounds can be

obtained bydirect bromination of ethylbenzene? Specify the reaction conditions.

1329. What reagents can be used to accomplish the following conversions?



1330*. Write the reaction of toluene chloromethylation by the Blanc ethod.

1331*. Indicate a method for preparing 2,5-dimethylbenzyl chloride from *p*-xylene.

1332. Using the reaction of chloromethylation, obtain the following compounds from benzene: (a) benzyl alcohol, (b) methylbenzyl ether, (c) phenylacetonitrile, (d) dimethylbenzylamine.

C. Properties

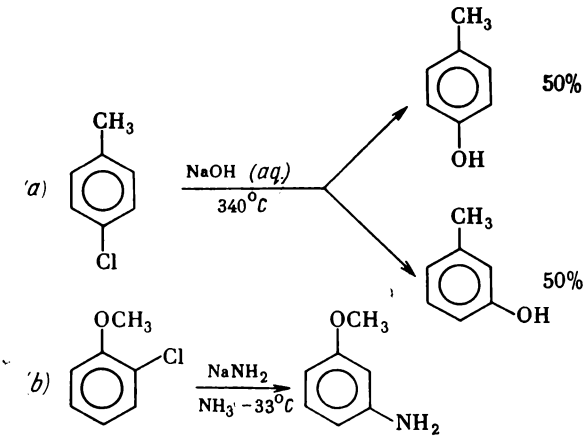
1333. Characterize the mutual effects that the chlorine atom and benzene ring produce on each other in a chlorobenzene molecule.

1334. Compare the structure of chlorobenzene and vinyl chloride. How do these compounds behave in nucleophilic substitution reactions?

1335. Give examples of nucleophilic substitution reactions of chlorine atom in chlorobenzene. Consider their mechanisms.

1336*. Explain why the nucleophilic substitution of chlorine atom is accompanied by partial or complete rearrange-

ment in the following reactions:



1337. What conditions are required for replacement of chlorine in chlorobenzene by the hydroxyl group? Indicate the importance of this reaction.

1338. Explain which of the following compounds: (a) chlorobenzene, (b) *p*-methoxychlorobenzene, is easier to react with sodium methoxide.

1339. Using isomers of nitrochlorobenzene as examples consider the effect of the nitro group on the affinity of the halogen for nucleophilic substitution. Write the reactions and consider their mechanism.

1340. Compare the mechanism of hydrolysis of *p*-nitrobromobenzene with that of ethyl bromide in an aqueous solution of NaOH. What are the differences?

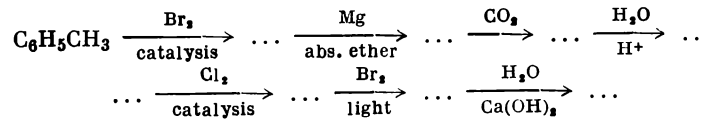
1341. Arrange the following compounds in the order of their increasing affinity for nucleophilic substitution of a bromine atom: (a) *p*-nitrobromobenzene, (b) bromobenzene, (c) *p*-bromotoluene. Develop your reasons.

1342. Use the Fittig-Wurtz method to obtain: (a) butylbenzene, (b) 1,6-diphenylhexane.

1343. Obtain 2,2'-dinitrodiphenyl by the Ullmann reaction.

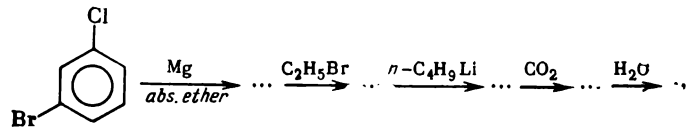
1344. What compounds are formed by the following con-

versions:



1345. Use the Grignard reaction to obtain (a) *p*-ethylbenzoic acid, (b) triphenylcarbinol, (c) di-*o*-tolylcarbinol.

1346*. Write formulas of the intermediate and end products of the following reactions:



1347. Compare the structure of benzyl chloride and allyl chloride. What accounts for the increased affinity of these compounds for nucleophilic substitution?

1348. Write the reactions of benzyl chloride with: (a) water, (b) ammonia, (c) sodium ethoxide, (d) silver acetate, (e) potassium cyanide. Name the reaction products and consider the mechanism of one of the reactions.

1349. Compare the structure of chlorobenzene and benzyl chloride, and also the activity of chlorine atom in these compounds in nucleophilic substitution reactions. Explain the differences.

1350. What reaction can be used to distinguish between benzyl chloride and *o*-chlorotoluene?

1351. Write the reactions of hydrolysis: (a) of *p*-bromotoluene, (b) of 2,4-dinitrobromobenzene, (c) of 1-bromo-1-phenylpropane. In what case will the hydrolysis be easier?

1352. Write the reactions of alkaline hydrolysis of each of the products of toluene chlorination into the side chain. Name the starting and end products.

1353. What compound is formed by the action of sodium metal on benzyl chloride? Obtain sym-diphenylethylene from the reaction product.

1354. Explain what hydrocarbons can be formed by the action of sodium metal on a mixture of bromobenzene and

propyl bromide. What hydrocarbon is predominantly formed?

1355. Complete the following:

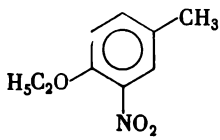
(a) $C_6H_5-CH_2Cl \xrightarrow[\text{abs. ether}]{Mg} \ldots \xrightarrow{CO_2} \ldots \xrightarrow[H^+]{HOH} \ldots$

(b) $C_6H_5-CH_2Cl \xrightarrow[\text{abs. ether}]{Mg} \ldots \xrightarrow{CH_3COC_2H_5} \ldots \xrightarrow[H^+]{HOH} \ldots$

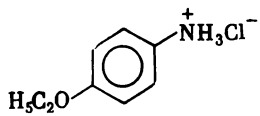
1356. Use benzene to prepare: (a) *p*-propylbenzoic acid, (b) phenylacetic acid.

1357. Use benzyl chloride to prepare: (a) methyl benzyl ether, (b) dibenzyl ether, (c) benzyl acetate, (d) phenylnitromethane, (e) phenylacetic acid, (f) phenylbenzylcarbinol.

1358. Suggest methods for preparing the following compounds:



from toluene (via halogenation into the ring)



from p-nitrochlorobenzene

D. Establishing the Structure of Organic Compounds by Their Properties

1359. Determine the structure of the compound $C_7H_6Cl_2$ that: (a) forms C_7H_6O by boiling with water in the presence of $Ca(OH)_2$, which, in turn, gives derivatives with hydroxylamine and phenylhydrazine, (b) turns into benzoic acid on oxidation with $KMnO_4$.

1360. Write a structural formula of the compound $C_7H_6Cl_2$ that is easily hydrolyzed with formation of a neutral product having the formula C_7H_7ClO and forms *m*-chlorobenzoic acid on oxidation.

1361. What is the structural formula of a compound having the composition $C_8H_6Cl_4$, the hydrolysis of which gives 3-methyl-4-chlorobenzoic acid?

1362. What is the structure of the compound C_6H_4BrCl that is treated with magnesium in ether, and then with carbon dioxide and dilute hydrochloric acid to give *m*-chlorobenzoic acid?

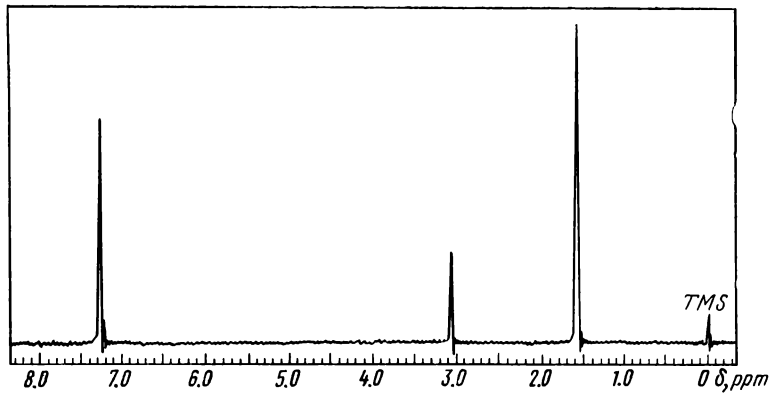


Fig. 38. NMR spectrum of $C_{10}H_{13}Cl$

1363*. Establish the structure of the compound $C_{10}H_{13}Cl$ that is oxidized into benzoic acid and has the NMR spectrum shown in Fig. 38.

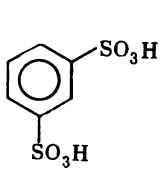
CHAPTER TWENTY

AROMATIC SULPHOACIDS

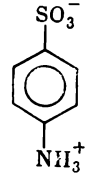
A. Isomerism. Nomenclature. Methods of Preparing

1364. Write structural formulas of the following compounds: (a) benzenesulphonic acid, (b) all isomers of toluenesulphonic acid, (c) sym-benzenetrisulphoacid.

1365. Name the following compounds:



a



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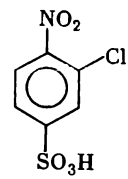

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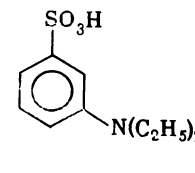


d

1366. Write the reaction of benzene sulphonation with sulphuric acid. Give the mechanism of the reaction. What side product is formed in the reaction?

1367. Compare the mechanism of sulphonation with that of other reactions of electrophilic substitution into the benzene ring, e.g. halogenation. Compare the structure of σ-complexes that are formed by these reactions and the kinetics of the processes.

1368*. Explain why the rate of nitration of hexadeuterobenzene and of ordinary benzene are equal, whereas the rate of sulphonation of deuterobenzene is slower than of ordinary benzene. Formulate the concept of kinetic isotope effect.

1369. Specify conditions for the formation of mono-, di-, and trisulphonic acids of benzene. Write the reactions.

1370. Write the reaction of monosulphonation of benzene, toluene, and nitrobenzene. In which case is the rate of sulphonation the highest?

1371. What sulphonating agents do you know? Write the reactions of sulphonation and chlorosulphonation for toluene and nitrobenzene.

1372. Write the reactions used for isolation of sulphonic acids from the reaction mixture.

1373*. During sulphonation of toluene with sulphuric acid at 0°C, 42 per cent of *ortho*-toluenesulphonic acid

and 54 per cent of *para*-isomer are formed. At 100°C, the quantities of the formed isomers are 13 and 79 per cent respectively. Explain.

1374. Suggest methods for preparing *o*-, *m*-, and *p*-chlorobenzenesulphonic acids from benzene.

1375. Compare the reactions for preparing the following compounds: (a) 4-nitro-2-toluenesulphonic acid from toluene, (b) 2-chloro-5-nitrobenzenesulphonic chloride from benzene.

B. Properties

1376. Consider the structure of the sulpho group and characterize its effect on the distribution of the electron density in the benzene nucleus. What kind of orientant is the sulpho group?

1377. Give examples of nucleophilic substitution reactions of hydrogen in the benzene nucleus of benzenesulphonic acid.

1378. Give examples of the following reactions for *para*-toluenesulphonic acid: (a) substitution of the nitrile group for the sulpho group, (b) substitution of the hydrogen atom for the sulpho group, (c) preparing any functional derivative.

1379. Write the reaction of alkaline fusion of sodium benzenesulphonate. Consider the mechanism of the reaction.

1380. Obtain the nitrile of *ortho*-toluyl acid from a potassium salt of *ortho*-toluenesulphonic acid. Compare the mechanism of this reaction with that of the alkaline fusion.

1381. Write the hydrolysis of benzenesulphonic acid. Consider the mechanism of the reaction.

1382. Write structural formulas of monosulphonic acids that are formed by sulphonation of each xylene isomer. Explain which isomer is the easiest to sulphonate.

1383*. Why is mesitylenesulphonic acid hydrolyzed much faster than 2,4,6-tribromobenzenesulphonic acid?

1384. Write the reactions for preparing the following derivatives of benzenesulphonic acid: (a) sodium salt, (b) a salt of *p*-toluidine, (c) an acid chloride (two methods), (d) an amide, (e) methyl ester (three methods).

1385. Figure 39 shows the I-R spectrum of benzenesulphochloride (liquid film). What frequencies are due to the

valence oscillations of the SO_2 group? Are these frequencies characteristic?

1386*. What compounds are formed from benzenesulphonyl chloride: (a) by reduction (Zn + HCl), (b) by the Friedel-Crafts reaction with benzene? Write the reactions.

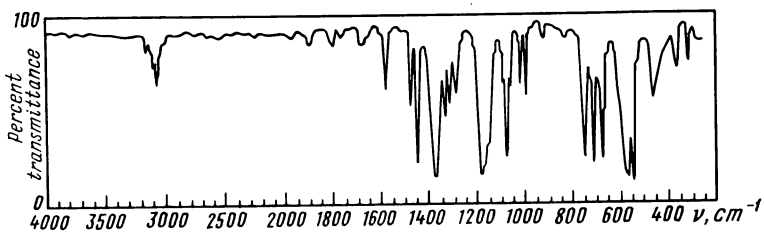


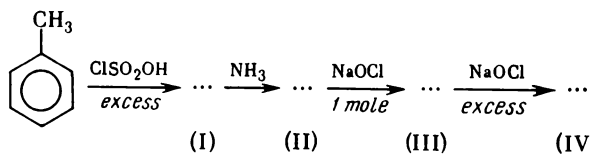
Fig. 39. I-R spectrum of benzene sulphochloride

1387. Write the synthesis of methyl ester of *p*-toluenesulphonic acid from toluene. Use the reactions with phenol and aniline to illustrate the use of this compound as a methylating agent.

1388*. Compare the structures of benzamide and benzenesulphonamide. What is the difference in chemical properties of these compounds?

1389. What principle is used in separation of primary, secondary and tertiary amines with benzene sulphochloride? Separate a mixture of mono-, di-, and triethylamines.

1390*. Fill in the missing formulas of the intermediate and end products into the following:

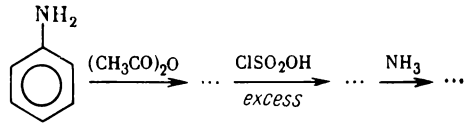


What is the practical importance of the products (III) and (IV)? Write the hydrolysis of the compound (III).

1391. Obtain the following compounds from *p*-toluenesulphonic acid: (a) toluene, (b) *p*-cresol, (c) *p*-toluic acid.

1392. Write the reaction for preparing sulphanilic acid from aniline. Explain its structure and properties.

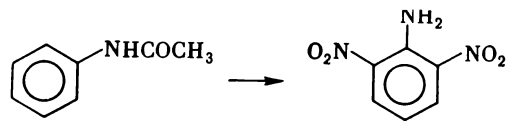
1393. Fill in the missing formulas of the intermediate and end products into the following:



1394. Use benzenesulphonic acid to obtain: (a) thiophenol, (b) diphenyl sulphide, (c) diphenyl sulphone.

1395*. Use phenol to obtain *o*-bromophenol free from the *para*-isomer.

1396*. Indicate the sequence of the reactions by which the following conversion can be accomplished:



(without formation of isomers). Write the reactions.

C. Establishing the Structure of Organic Compounds by Their Properties

1397. Establish the structure of $C_7H_8O_3S$ the oxidation of which with potassium permanganate gives sulphobenzoic acid and fusion with sodium hydroxide gives *o*-cresol.

1398. Write a structural formula of the compound $C_8H_{10}O_3S$ the oxidation of which gives sulphobenzoic acid and alkaline fusion gives *p*-ethylphenol.

1399. Oxidation of the compound $C_7H_7ClO_3S$ gives sulphobenzoic acid, and halogenation in the presence of a catalyst gives only one monohalogen derivative. Write the structural formula of the compound $C_7H_7ClO_3S$.

1400*. Write all possible structural formulas for the compound $C_7H_7BrO_3S$ that possesses the following properties: (a) when desulphonated, it gives *o*-bromotoluene, (b) oxida-

tion gives the acid $C_7H_5BrO_5S$, the heating of which with solid alkali gives *m*-bromophenol.

1401*. The substance $C_8H_9ClO_3S$ has the following properties: (a) when treated with superheated steam, it converts into *o*-chloroethylbenzene, (b) its oxidation gives an acid, the alkaline fusion of which gives resorcinol (*m*-dihydroxybenzene). Write possible structural formulas for the substance $C_8H_9ClO_3S$.

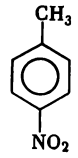
1402*. Establish the structure of the compound $C_8H_{10}O_3S$ the alkaline hydrolysis of which gives the salt $C_7H_7O_3SNa$. The latter is fused with sodium hydroxide to give *p*-cresol.

CHAPTER TWENTY-ONE

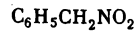
AROMATIC NITRO COMPOUNDS. INTERMEDIATE PRODUCTS OF REDUCTION OF NITRO COMPOUNDS

A. Isomerism. Nomenclature. Methods of Preparing

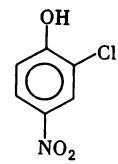
1403. Name the following compounds



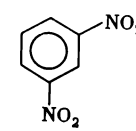
a



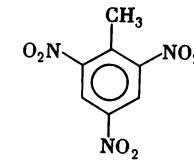
b



c



d



e

1404. Write the structural formulas of: (a) *o*-nitrotoluene, (b) *p*-nitroethylbenzene, (c) sym-trinitrobenzene, (d) methylphenylnitromethane, (e) 2,4,6-trinitrophenol.

1405. Give the structural formulas of all isomers of aromatic nitro compounds having the composition $C_7H_7NO_2$. Name them.

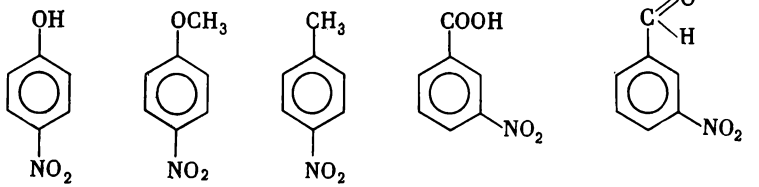
1406. Write the reaction of nitration of benzene with a nitrating mixture. Consider the mechanism of the reaction. Characterize the role of sulphuric acid in the reaction.

1407*. Why does the rate of nitrobenzene nitration with the nitrating mixture increase 1000 times if 90 per cent sulphuric acid is used instead of 80 per cent acid?

1408*. Why is it possible to obtain mononitro compounds containing insignificant amounts of polynitro compounds by nitrating aromatic compounds, whereas sulphonation, in addition to monosulphonic acid, gives also appreciable quantity of disulpho derivatives?

1409*. What nitrating agents are used to introduce the nitro group into the aromatic ring? Which of them is more

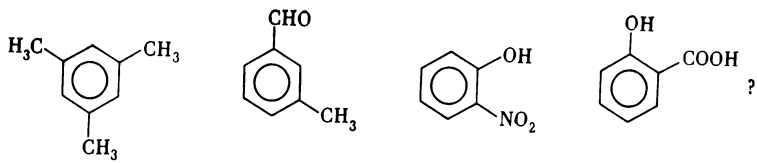
suitable in the synthesis of each of the following nitro compounds:



a *b* *c* *d* *e*

1410. Write the reaction of mononitration into the ring of: (a) ethylbenzene, (b) isopropylbenzene, (c) benzoic acid, and (d) *p*-nitrobromobenzene. Indicate the compounds that easily enter the reaction.

1411. How will nitration into the ring of the following compounds occur:



a *b* *c* *d*

Indicate the compounds with concerted orientation of the substitutes.

1412. What dinitro compound and why can be easier converted into the corresponding trinitro derivative: 1,3-dinitrobenzene or 2,4-dinitrotoluene?

1413. What compound will be obtained by the action of dilute HNO_3 on toluene with heating? Give the mechanism of the reaction.

1414. Obtain phenylnitromethane from benzyl chloride.

B. Properties

1415. Consider the structure of the nitro group and its effect on the direction and the rate of electrophilic substitution in the aromatic ring.

1416. Who was the first to reduce nitrobenzene to aniline? When did it happen? What is the importance of this discovery? Indicate the reductants that are used for commercial conversion of nitro compounds into amines.

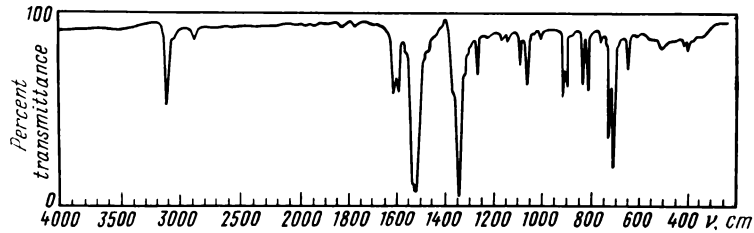


Fig. 40. I-R spectrum of *m*-dinitrobenzene

1417. Calculate the number of grams of iron that are required to reduce 100 g of nitrobenzene to aniline in a neutral medium.

1418. What reagents are required to reduce *m*-dinitrobenzene to: (a) *m*-phenylenediamine, (b) *m*-nitroaniline? Write the reaction equations.

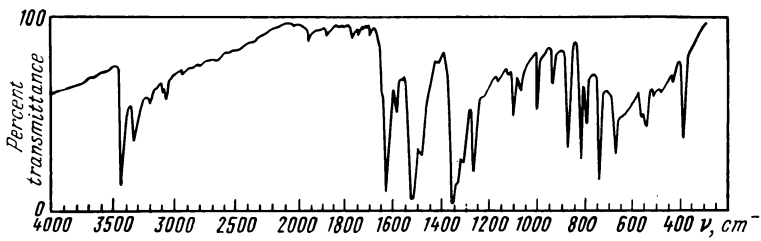


Fig. 41. I-R spectrum of reduction product of *m*-dinitrobenzene

1419. Figure 40 gives the I-R spectrum of *m*-dinitrobenzene (KBr plate). How will the spectrum change if *m*-dinitrobenzene is reduced to: (a) *m*-nitroaniline, (b) *m*-phenylenediamine? To what product of reduction of *m*-dinitrobenzene does the I-R spectrum shown in Fig. 41 (KBr plate) correspond?

1420. Write a balanced equation for the reaction of nitrobenzene, and also sym-trinitrobenzene, with sodium hydro-

xide in the presence of potassium ferricyanide. What is the mechanism of these reactions? Which of the two substances is more active in this reaction? What kind of orientant is the nitro group in this case?

1421. Write structural formulas of all isomers of dinitrobenzene. Explain which of them will enter the reactions of nucleophilic substitution of the nitro group? Give examples.

1422. Explain the differences in the acid properties of *m*- and *p*-nitrophenols (pK_a = 8.00 and 7.21 respectively).

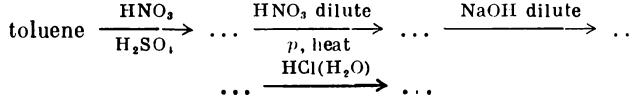
1423. Arrange the following compounds in the order of their increasing basic properties: (a) aniline, (b) *p*-nitroaniline, (c) 2,4,6-trinitroaniline. Explain.

1424. Consider the effect of the nitro group on the activity of the methyl group hydrogen in *o*-nitrotoluene. Write the reaction of propionic aldehyde with *o*-nitrotoluene. Will toluene enter the reaction with this aldehyde?

1425. What accounts for the activity of hydrogen of the phenylnitromethane methylene group? Give tautomeric forms of phenylnitromethane. What is the structure of their common mesomeric ion?

1426. What is known as 'pseudo acids'? How do they differ from true acids? What isomer of aromatic nitro compounds having the composition $C_7H_7NO_2$ is a pseudo acid?

1427. Complete the following:

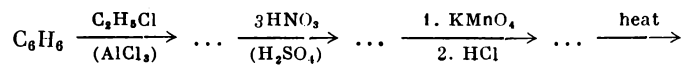


Why does phenylnitromethane easier react with alkali than 1-nitro-2-phenylethane?

1428. Which of the following compounds: (a) nitroethane, (b) 2-nitro-2-methylbutane, (c) nitro-cyclohexane, (d) nitrobenzene, (e) 1-nitro-1-phenylethane, will react with aqueous solutions of alkalis? Write the reactions.

1429. By what reactions can phenylnitromethane be distinguished from *o*-nitrotoluene? Suggest a chemical method for the separation of these compounds.

1430. Write structural formulas of the intermediate and end products in the following:



1431. Use toluene to obtain *o*-, *m*-, and *p*-nitrobenzoic acids.

1432. Use toluene to synthesize: (a) *m*-aminobenzoic acid, (b) *p*-aminobenzoic acid.

1433. Use toluene to obtain sym-trinitrobenzene.

1434*. Suggest methods to synthesize: (a) 3,5-dinitrotoluene, (b) 2,6-dinitrotoluene from toluene.

1435. Name the intermediate products of nitrobenzene reduction: (a) C_6H_5NO, (b) $C_6H_5NH(OH)$, (c) $C_6H_5-N=\underset{\displaystyle O}{\downarrow}N-C_6H_5$, (d) $C_6H_5NH-NH-C_6H_5$, (e) $C_6H_5-N=N-C_6H_5$. Specify the conditions for reactions by which these compounds are obtained.

1436*. Complete the following:

(a) $C_6H_5NO_2+2Zn+4NH_4Cl \longrightarrow \ldots$

(b) $4C_6H_5NO_2+3CH_3ONa \longrightarrow \ldots$

Name the obtained compounds.

1437. Suggest a method of synthesizing *m*-chlorophenylhydroxylamine from benzene.

C. Establishing the Structure of Organic Compounds by Their Properties

1438. Establish the structure of the compound $C_8H_9NO_2$ that does not react with aqueous solution of alkali, and is brominated in the presence of iron to give only one monobromo derivative.

1439. A substance having the composition $C_8H_9NO_2$ is acted upon with NaOH to give $C_8H_8NO_2Na$, and oxidized into terephthalic acid. What is the structure of $C_8H_9NO_2$?

1440. Determine the structure of $C_7H_7NO_2$ that is chlorinated, in the absence of catalysts, into $C_7H_4Cl_3NO_2$ that, in turn, is hydrolyzed into *p*-nitrobenzoic acid. Synthesize the compound from benzene.

1441*. *o*-Nitrochlorobenzene was used to obtain the compound $C_6H_6N_2O_2$. Establish its structure by the I-R spectrum (KBr plate, Fig. 42). Write the reaction and specify the conditions.

1442*. Determine the structure of an aromatic compound having the composition $C_6H_4ClNO_2$ that does not react, under normal conditions, with alkali or ammonia.

1443. Establish the structure of the compound $C_7H_6BrNO_2$. When heated in normal conditions with an aqueous solution of alkali, it gives a neutral product having the composition $C_7H_7NO_3$, and is oxidized into *p*-nitrobenzoic acid.

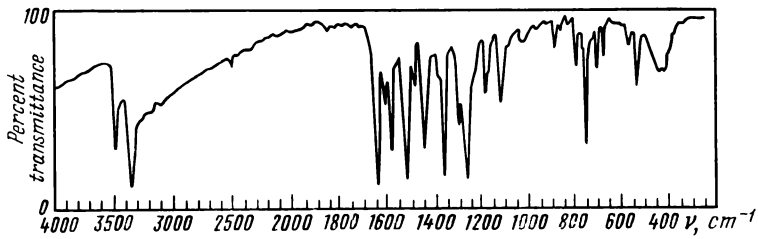


Fig. 42. I-R spectrum of $C_6H_6N_2O_2$

1444. Establish the structure of the substance $C_6H_4N_2O_4$. When heated with ammonia it gives $C_6H_6N_2O_2$ that is monohalogenated into only one isomer.

1445*. What structure can the compound $C_7H_6N_2O_4$ with the following properties have: (1) when nitrated in the presence of oleum it gives one product, (2) it is oxidized to give the acid $C_7H_4N_2O_6$ that is heated with lime to give $C_6H_4N_2O_4$. The latter is reduced with sodium sulphide to *m*-nitroaniline.

1446*. A substance having the formula $C_6H_4N_2O_7S$ has the following properties: (a) by the action of superheated steam in the presence of sulphuric acid, it gives *m*-dinitrobenzene, (b) its bromination gives only one isomer. What is the structure of the compound?

1447. Establish the structure of the compound $C_{14}H_{14}N_2O$. The substance is pale yellow, and its other properties are as follows: (1) under the action of zinc dust, in the presence of NaOH, it first turns into the compound $C_{14}H_{14}N_2$ (yellow) and then into a colourless compound $C_{14}H_{16}N_2$, (2) it gives *p*-toluidine by the action of tin in hydrochloric acid.

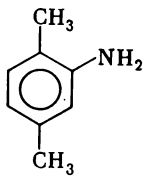
CHAPTER TWENTY-TWO

AROMATIC AMINES

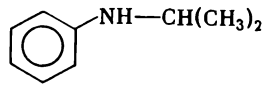
A. Isomerism. Nomenclature

1448. Write the structural formulas of all isomers of an aromatic amine having the composition C_7H_9N. Name them.

1449. Name the following amines:



a



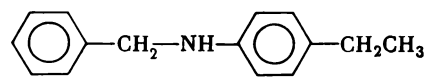
b

$(C_6H_5)_2NCH_3$

c

$(p\text{-}CH_3C_6H_4)_3N$

d



e

1450. Write the structural formulas of the following compounds: (a) *p*-toluidine, (b) nitroaniline, (c) *o*-phenylenediamine, (d) *o*-anizidine, (e) *p*-phenetidine, (f) sym-tribromoaniline, (g) N-benzyl-N-ethylaniline, (h) benzidine.

B. Methods of Preparing

1451. Write the reactions used for commercial manufacture of aniline.

1452. What derivatives of aromatic hydrocarbons can be used for the manufacture of aromatic amines? Give the reactions for preparing *p*-toluidine.

1453. Name the most important reductants used for preparing amines from nitro compounds. What reagents are required to convert *m*-dinitrobenzene into: (a) *m*-phenylenediamine, (b) *m*-nitroaniline?

1454*. Write the reactions of reduction of: (a) *p*-nitrotoluene with stannous chloride in hydrochloric acid, (b) 2,4-

dimethylnitrobenzene with hydrogen on a nickel catalyst, (c) *p*-nitroaniline with hydrazine in the presence of Raney nickel, (d) *m*-nitrobenzene with sodium sulphide in an aqueous medium.

1455. What compounds can be obtained by reduction of *m*-nitrobenzenesulphonic acid in an alkaline medium? Write the reactions.

1456. Suggest a method for synthesis of 2,4-diaminotoluene from benzene.

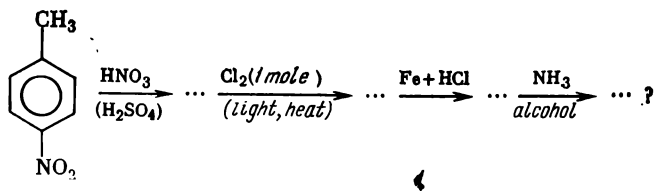
1457. Obtain *m*-aminophenol from benzenesulphonic acid.

1458*. How can 2,4,5-triaminonitrobenzene be synthesized from *m*-dichlorobenzene?

1459. Using *o*-toluidine, synthesize the following secondary and tertiary amines: (a) N,N-diethyl-*o*-toluidine, (b) N-benzyl-*o*-toluidine, (c) N,N-diphenyl-*o*-tolylamine.

1460. By the action of what reagents and in what conditions can benzylamine be obtained: (a) from phenylnitromethane, (b) from benzyl chloride, (c) from benzonitrile, (d) from benzaldehyde? Write the reactions.

1461. What compound is formed by the following conversions:



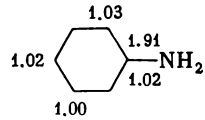
1462. Write the reactions for preparing all isomers of phenylenediamine from benzene.

C. Properties

1463. Consider the structure of an aniline molecule. In what direction is the electron density displaced in the molecule of this compound?

1464*. Calculations by the molecular orbital method give the following distribution of π-electron density in the mole-

cule of aniline:



Use these data to characterize the mutual effects that the amino group and benzene ring produce on each other.

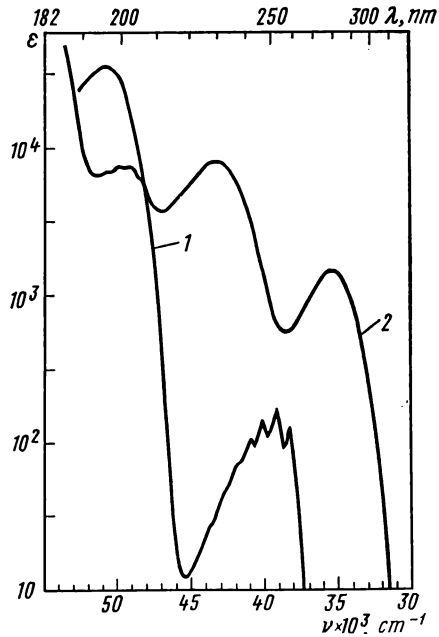


Fig. 43. U-V spectra of aniline and its salt

1465. Figure 43 gives U-V spectra of aniline and its salt. Identify the curves. Develop your reasons.

1466. Consider the I-R spectrum of aniline (Fig. 44, liquid film). Indicate characteristic frequencies of the amino group and of the benzene ring.

1467. Characterize the basic properties of aniline. Explain the difference in the basic properties of aniline ($pK_b = 9.4$) and methylamine ($pK_b = 3.4$).

1468. Formulate the general principles characterizing the effect of substitutes in the ring on the basic properties of aromatic amines. Arrange the following amines in the

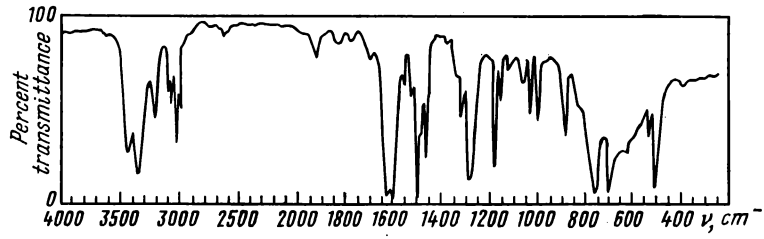


Fig. 44. I-R spectrum of aniline

order of their increasing basicity: (a) aniline, (b) benzylamine, (c) *p*-anizidine, (d) *p*-nitroaniline.

1469. Explain variations of the basic properties in the following series: (a) aniline, (b) diphenylamine, (c) triphenylamine.

1470. Write the reactions for preparing: (a) aniline hydrochloride, (b) *o*-toluidine hydrobromide, (c) *p*-anizidine bisulphate. Write balanced equations for the reactions of isolation of free bases from these salts.

1471. What compounds are formed from *p*-toluidine by the action on it with: (a) acetic anhydride, (b) *p*-toluene sulphochloride? Characterize basic properties of the reaction products.

1472. What compound is formed by heating monoethylaniline with acetic anhydride? What reaction will occur with heating the obtained compound with dilute alkali solution?

1473. Obtain the following compounds from aniline:

(a) C_6H_5NHCHO

(b) $C_6H_5NHCOC_6H_5$

(c) $C_6H_5NHSO_2C_6H_5$

(d) $C_6H_5NHCOCOOH$

Name them. Indicate the compound in which the hydrogen atom of the NH group has the highest acidity.

1474. What compound is formed by the following conversions?

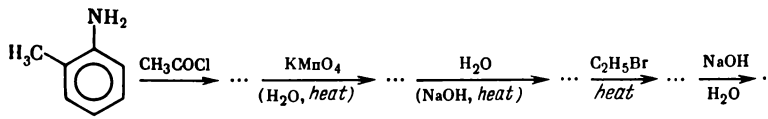
$$C_6H_5NH_2 \xrightarrow{C_6H_5SO_2Cl} \cdots \xrightarrow[H_2O]{NaOH} \cdots \xrightarrow{(CH_3O)_2SO_2} \cdots \xrightarrow[NaOH,\ heat]{H_2O} \cdots$$

1475. What compounds can be formed by heating *p*-toluidine with ethyl bromide? Consider the mechanism of these reactions.

1476. What products are formed by heating aniline with excess methyl alcohol in the presence of a small amount of concentrated sulphuric acid in an autoclave to 230°C? How can the main reaction product be isolated?

1477. What is the structure of the compound that is formed by heating aniline with 2,4-dinitrochlorobenzene? Explain the mechanism of the reaction.

1478. Complete the following:

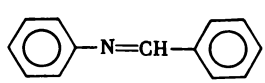


1479. Give examples of reactions: (a) of N-acylation of *p*-anizidine, (b) of N-alkylation of *p*-anizidine, and (c) of N-arylation of *p*-anizidine. Explain the mechanism of conversions (a) and (b). To what classes of compounds can the reaction products be attributed?

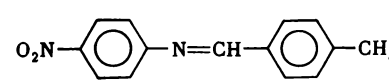
1480. How can a mixture of amines containing *p*-toluidine, N-benzylaniline, and diethylaniline be separated?

1481. Which of the following amines will give the isonitrile reaction: (a) *m*-toluidine, (b) N-butylaniline, (c) dimethylaniline? Write the reactions.

1482. Obtain the following Schiff bases:



a



b

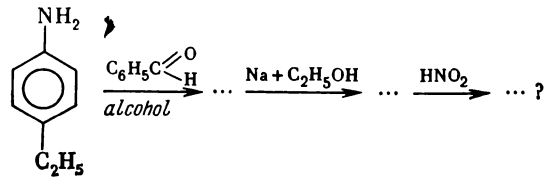
Explain the mechanism of formation of the compound (a).

1483. How will the following amines react with nitrous acid: (a) *o*-toluidine, (b) benzylamine, (c) ethylaniline, (d) dimethylaniline, (e) triethylamine? Name the reaction products.

1484. Compare the attitude of primary fatty and aromatic amines to nitrous acid. Give examples.

1485. What is the attitude of tertiary fatty amines and tertiary fatty aromatic amines to nitrous acid? Write the reaction of diethylaniline with nitrous acid and consider its mechanism.

1486. What compounds are formed by the following conversions:



1487. By what reactions can the following isomers be distinguished: (a) *m*-ethylaniline and N-ethylaniline, (b) 2,6-dimethylaniline and N,N-dimethylaniline, (c) N-ethylaniline and N,N-dimethylaniline?

1488. What kind of orientant is the amino group in a neutral or acid medium? Give examples of reactions of electrophilic substitution for *o*-toluidine. What effect does acylation of the amino group produce on the direction and the rate of electrophilic substitution?

1489. Compare and explain the attitude of aniline and acetanilide to bromine. What are the main products of these reactions?

1490. Formation of what product should be expected from the action of the nitrating mixture on aniline? Write the reaction.

1491*. Obtain *m*-nitroaniline from: (a) aniline, (b) *m*-dinitrobenzene. What method of preparing *m*-nitroaniline is more efficient and why?

1492*. The dimethylamino group orients in the ortho and para positions. Why is *m*-nitrodimethylaniline predo-

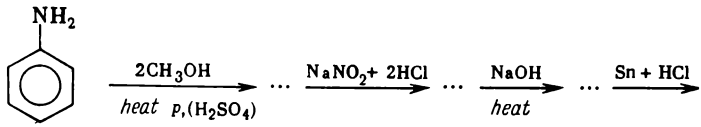
minantly formed in the nitration of dimethylaniline in concentrated sulphuric acid?

1493. How can *p*-nitroaniline be obtained from aniline? Give the mechanisms of all reactions used.

1494. How can 3-nitro-4-aminotoluene be synthesized from *p*-toluidine?

1495. Obtain sulphanilic acid from aniline. Give the reactions illustrating its amphoteric properties.

1496. What compounds are formed by the following conversions:

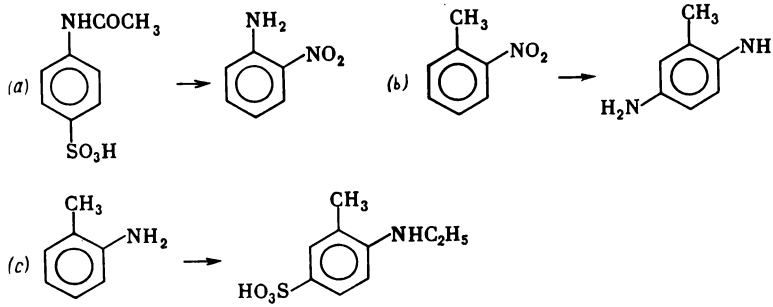


1497*. Obtain *p*-bromoaniline from aniline.

1498. Obtain ethyl hydrochloride of *p*-aminobenzoic acid from *p*-nitrotoluene.

1499*. Obtain β-phenylethylamine from benzaldehyde and malonic ester.

1500. How can the following conversions be accomplished:



D. Intramolecular Rearrangements

1501. Write the reaction by which hydrazobenzene is converted into benzidine. Specify the reaction conditions.

1502. Write the benzidine rearrangement of *o*,*o*′-hydrazotoluene. Consider the mechanism of the reaction.

1503*. Write the structural formula of the hydrazo compound the benzidine rearrangement of which gives 2,2′-dimethoxy-4,4′-diaminodiphenyl.

1504. What conversions do the following compounds undergo when heated in an acid medium: (a) *o*,*o*′-diethoxyhydrazobenzene, (b) *p*-chlorohydrazobenzene, (c) *p*,*p*′-hydrazotoluene?

1505. What compound is formed by heating *N*-methylaniline hydrochloride in a sealed vessel to 350°C? Write the reaction and explain its mechanism.

1506*. When N-isobutylaniline hydrochloride is heated, it gives *p*-amino-*tert*-butylbenzene. Write the reaction.

1507. What compound is formed by heating phenylhydroxylamine in dilute sulphuric acid? Consider the reaction mechanism?

1508. Electrochemical reduction of nitrobenzene in 80 per cent sulphuric acid gives *p*-aminophenol. Give the main stages of the process.

1509*. What compounds are formed from phenylhydroxylamine by the action of sulphuric acid in the presence of excess amounts of the following compounds: (a) ethyl alcohol, (b) phenol, (c) aniline? What is the mechanism of these reactions?

1510*. Obtain *p*-nitrosodiphenylamine from diphenylamine.

E. Establishing the Structure of Organic Compounds by Their Properties

1511*. Establish the structure of the aromatic compound $C_8H_{11}N$ by its I-R spectrum (liquid film, Fig. 45).

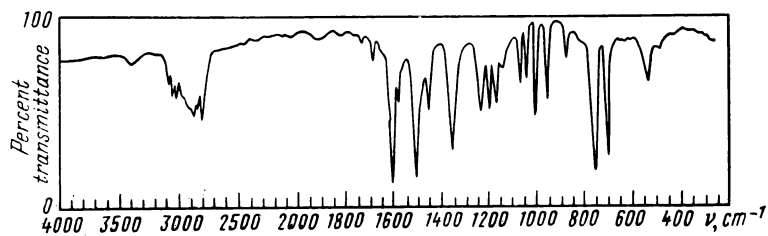


Fig. 45. I-R spectrum of $C_8H_{11}N$

1512*. Establish the structure of the substance $C_8H_{11}N$. It gives salts with acids, reacts with HNO_2 to give $C_8H_{10}N_2O$ that, in turn, is decomposed by alkali with heating to give dimethylamine and *p*-nitrosophenol.

1513. Write the structural formula of the compound $C_8H_{11}N$ having a strong basic character and giving the neutral compound $C_8H_{10}O$ by reaction with nitrous acid. Oxidation of $C_8H_{10}O$ gives isophthalic acid.

1514*. Establish the structure of the compound C_7H_9N the U-V spectrum of which only slightly differs from that of benzene, and the I-R spectrum has absorption bands at 3370 and 3290 cm^{-1}.

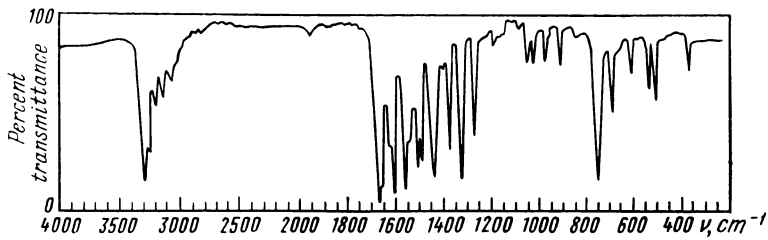


Fig. 46. I-R spectrum of C_8H_9NO

1515*. What chemical conversion has aniline undergone if the resultant compound, C_8H_9NO, has the I-R spectrum shown in Fig. 46 (KBr plate)?

1516*. Establish the structure of the compound $C_9H_8Cl_3NO$. It does not react with acids and when heated with aqueous solutions of alkali, it gives a mixture of salts of *p*-aminobenzoic and acetic acids. Suggest a method to synthesize $C_9H_8Cl_3NO$ from toluene.

1517*. Establish the structure of a neutral compound having the composition $C_9H_{11}NO_4S$ that gives a mixture of salts of sulphanilic and acetic acids on heating with alkali solution.

1518*. Write the structural formulas of aromatic amines having the composition $C_{11}H_{17}N$ and containing five methyl groups. Which of these amines does not react with acetic anhydride or nitrous acid?

1519*. Write the structural formula of the compound $C_8H_8N_2O_3$ that does not give salts with acids; when reduced with subsequent acetylation it gives a diacetyl derivative of *p*-phenylenediamine. Obtain the compound $C_8H_8N_2O_3$ from benzene.

1520*. Establish the structure of the compound $C_8H_{11}N$ that reacts with nitrous acid in the cold to give a neutral

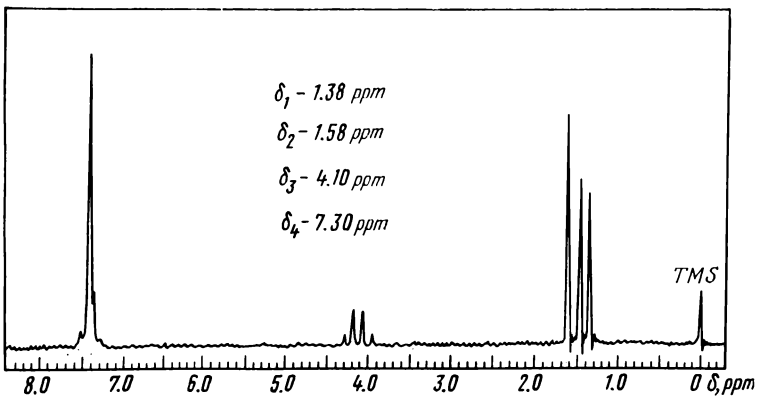


Fig. 47. NMR spectrum of $C_8H_{11}N$

compound having the composition $C_8H_{10}O$. The NMR spectrum of $C_8H_{11}N$ is given in Fig. 47.

1521*. Establish the structure of a colourless compound having the composition $C_{12}H_{12}N_2$ that: (a) does not give diazo compounds, (b) is easily oxidized into a yellow product having the formula $C_{12}H_{10}N_2$, (c) reacts with a mineral acid to turn into a compound having the same composition that gives *bis*-diazo compound.

1522*. Establish the structure of the compound $C_{14}H_{14}N_2O_3$ that is easily reduced with zinc in an alkaline medium first to $C_{14}H_{14}N_2O_2$ and then to $C_{14}H_{16}N_2O_2$. The latter reacts with a mineral acid to give 3,3′-dimethoxybenzidine.

CHAPTER TWENTY-THREE

DIAZO AND AZO COMPOUNDS

A. Preparing Diazo Compounds

1523. What is the diazotization reaction? Specify its conditions. Write the reaction of aniline diazotization in hydrochloric acid medium.

1524. Indicate which of the following amines can give diazonium salts: (a) *p*-toluidine, (b) N-ethylaniline, (c) propylamine, (d) sulphanilic acid, (e) cyclohexylamine, (f) dimethylaniline, (g) *o*-chloroaniline, (h) benzylamine.

1525. Write the structural formulas of the following compounds: (a) phenyldiazonium chloride, (b) *p*-nitrophenyldiazonium bromide, (c) *o*-methoxyphenyldiazonium bisulphate. Give the reactions by which these compounds are prepared.

1526. Write the reaction of diazotization of *p*-toluidine in hydrochloric acid. Consider the mechanism of the reaction. In what form do amine and nitrous acid react? What is the role of the mineral acid?

1527. Compare the action of nitrous acid in hydrochloric acid medium on cyclohexylamine and aniline at 0-5°C. Explain why the formed compounds belong to different classes.

1528. Write the reaction and explain the mechanism of benzidine diazotization in sulphuric acid medium.

1529. What diazotizing agents can nitrous acid form in hydrochloric acid medium? Give the reactions. Characterize the strength of the diazotizing agents.

1530*. What conditions are required to diazotize (a) *p*-toluidine, (b) 2,4,6-trinitroaniline?

1531. How can a salt of diazonium be obtained in the solid state? Write the reaction.

B. Properties of Diazo Compounds

1532. What is the structure of diazonium salts? Indicate the commonness and differences in the structure and properties of diazonium and ammonium salts.

1533. Write the reaction by which *p*-chlorophenyldiazonium chloride is converted into other products by subsequent action of a weak base (damp silver oxide), and then a strong base (NaOH). Name all forms of the diazo compounds.

1534. What diazo compounds are known as diazotates? Characterize their structure. What conditions are required for their formation? Give examples.

1535. What conversions do syn- and anti-diazotates undergo under the action of mineral acids? Write reactions for syn- and anti-*p*-bromophenyldiazotates of sodium.

1536. Using *m*-nitrophenyldiazonium chloride as an example, show the conversions that diazo compounds undergo with changing pH of the medium. Name all forms of the diazo compounds.

1537. Write the structural formulas of: (a) *p*-ethylphenyldiazonium chloride, (b) *p*-nitrophenyldiazonium hydroxide, (c) phenyldiazo acid, (d) potassium *m*-bromophenyldiazotate, (e) phenylnitrosoamine. In what solution (acid, neutral or alkaline) will most likely each of these compounds exist?

1538*. Write reactions for preparing a sodium salt of *p*-nitrophenyldiazo acid from *p*-nitroaniline and its conversion into a diazonium salt.

1539. What compound is formed by heating an aqueous solution of phenyldiazonium bisulphate? Explain the mechanism of the reaction.

1540. Write reactions for preparing phenol through a diazonium salt and also by alkaline fusion of a salt of benzenesulphonic acid. When is it reasonable to introduce an oxy group into the aromatic ring by decomposing diazonium salts? Give examples.

1541*. Which of the following compounds: (a) *m*-nitrophenol, (b) *p*-cresol, (c) *p*-chlorophenol, (d) resorcinol, should preferably be obtained by hydrolysis of the corresponding diazotized amines, and which by the alkali fusion? Write the reactions.

1542. Obtain *p*-nitrophenol from aniline.

1543*. Why is anisole also formed (in addition to phenol) in thermal decomposition of phenyldiazonium chloride in an aqueous-methanol medium?

1544*. Obtain guaiacol (pyrocatechol monomethyl ester) from *o*-nitrochlorobenzene.

1545. Write the synthesis of *m*-nitrophenetol from *m*-nitroaniline.

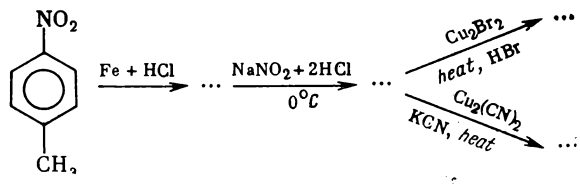
1546. By the action of what reagent can fluorine be substituted for the diazonium group? Write the reaction of preparing fluorobenzene from aniline. Explain the mechanism of the reaction.

1547*. Alongside with fluorobenzene, 3-nitrobiphenyl is also formed by heating phenyldiazonium borofluoride in a medium of nitrobenzene. Explain.

1548. Specify the conditions for substitution of chlorine or bromine for the diazonium group (Sandmeyer's reaction). Give examples.

1549. Obtain *o*-chlorotoluene from *o*-toluidine. Consider the mechanism of the last stage.

1550. Complete the following:



What is the role of cuprous salts at the last stage of the conversion?

1551. Synthesize *m*-bromoaniline from *m*-nitroaniline.

1552. Obtain *o*-toluic acid from toluene.

1553. Write the synthesis of *o*-chlorobenzoic acid from *o*-toluidine.

1554. Specify the conditions for replacement of the diazonium group by iodine. Consider the mechanism of this reaction using the reaction of preparing *p*-iodotoluene as an example. Why are copper salts not required in this case?

1555*. Suggest a method for preparing *m*-iodochlorobenzene from benzene.

1556. What is known as the deamination reaction? Specify the conditions of the reaction. What is the role of this reaction? Give examples.

1557*. What two competing reactions occur during heating a solution of diazonium salts with alcohols? Indicate the factors promoting each of these reactions.

1558. Suggest a method to synthesize sym-tribromobenzene from benzene.

1559*. Obtain 2,4,6-tribromobenzoic acid from *m*-nitrobenzoic acid.

1560. Obtain *m*-toluidine from *p*-toluidine (use the reaction of deamination at one stage).

1561. Accomplish the following conversions:

$$C_6H_5NH_2 \xrightarrow[0^\circ]{NaNO_2+2HCl} \ldots \xrightarrow{HgCl_2} \ldots \xrightarrow[heat]{2Cu} \ldots$$

1562. Use the Nesmeyanov method to obtain the following organometallic compounds: (a) *p*-hydroxyphenylmercury chloride, (b) *p*-carboethoxyphenylmercury chloride.

1563*. If aniline is diazotized in the absence of sufficient mineral acid, a bright yellow precipitate is formed instead of the clear solution of the diazonium salt. What is the structure of this yellow compound? Write the reaction of its formation.

1564. What compound is formed by reduction of phenyldiazonium chloride ($SnCl_2$ + HCl)? Write the reaction.

1565. Accomplish the following conversions:

$$C_6H_5NH_2 \xrightarrow[0^\circ]{NaNO_2+2HCl} \ldots \xrightarrow[(SnCl_2+HCl)]{[H]} \ldots \xrightarrow[(H_2O)]{NaOH} \ldots$$

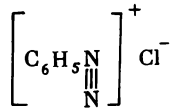
$$\ldots \xrightarrow{C_6H_5CHO} \ldots$$

1566. Write the reaction of preparing: (a) *m*-nitrophenol from *m*-dinitrobenzene, (b) nitrile *p*-nitrobenzoate from benzene, (c) *m*-toluic nitrile from toluene, (d) *m*-dibromobenzene from *p*-nitroaniline, (e) sodium anti-*p*-methoxyphenyldiazotate from anisole, (f) 2,4-dinitrophenylhydrazine from benzene.

C. Azo Coupling Reactions. Azo Dyes

1567. What is known as the azo coupling reaction? Give reactions of phenyldiazonium chloride with (a) phenol, (b) dimethylaniline.

1568. How do diazo and azo compounds differ from each other? Which of the following formulas belong to diazo and



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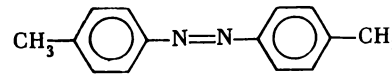

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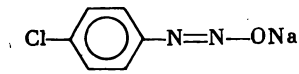

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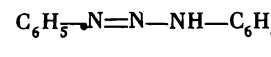

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which to azo compounds? Name them.

1569. Which of the following compounds: (a) dimethylaniline, (b) benzenesulphonic acid, (c) salicylic acid, (d) *m*-nitrotoluene, (e) picric acid, (f) *p*-ethylphenol, can be coupled with phenyldiazonium chloride? Write the reactions.

1570. Write the reaction of azo coupling of *p*-nitrophenyldiazonium with dimethylaniline, and also with phenol. Explain the mechanisms of the reactions.

1571. In what form do diazo compounds react with aromatic amines and phenols? To what type of reactions (with respect to the mechanism) can azo coupling be attributed? Give examples.

1572. Explain in what medium should diazonium salts be coupled with phenols? with amines?

1573*. Name the intermediate and end products of the following conversions:

$$(C_6H_5N_2)^+Cl^- \xrightarrow[(CH_3COONa),\ 0^\circ]{C_6H_5NH_2} \ldots \xrightarrow[(H_2O,\ 30^\circ)]{H_2SO_4} \ldots$$

1574. Characterize the effect of substitutes in the benzene ring of diazo compounds on the rate of the coupling reaction. Give examples.

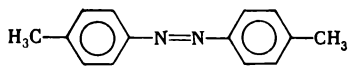
1575*. Write the structural formulas of diazonium cations that are formed during diazotization of the following amines: (a) aniline, (b) *p*-toluidine, (c) *p*-nitroaniline. Arrange these cations in the order of their decreasing electrophilicity. With what diazonium cation will the rate of coupling of phenol be the highest and why?

1576*. Why is mesitylene coupled with 2,4,6-trinitrophenyldiazonium bisulphate? Write the reaction.

1577. Give examples of the following compounds: (a) an aromatic amine that is diazotized easier than aniline, (b) a substituted phenol that does not enter azo coupling reactions, (c) substituted phenyldiazonium chloride that is more active in azo coupling than phenyldiazonium chloride, (d) an aromatic hydrocarbon capable of azo coupling with most active salts of diazonium.

1578. What azo compounds are known as azo dyes? What are diazo- and monoazo-components of the dye?

1579. Which of the following azo compounds are



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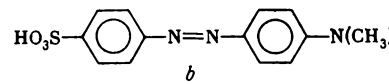

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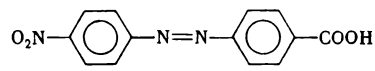

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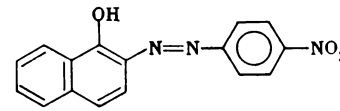

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azo dyes? What diazo- and monoazo-components should be taken to prepare these azo dyes? Write the reactions.

1580. Write reactions for the synthesis of the following azo dyes: (a) mordant yellow (diazo-component, *m*-nitroaniline; monoazo-component, salicylic acid), (b) methyl red (diazo-component, anthranilic acid; monoazo-component, N,N-dimethylaniline).

1581. Write the synthesis of azo dyes from the following pairs of compounds: (a) 2,4-dinitroaniline and *o*-cresol, (b) *o*-toluidine and phenol, (c) *p*-aminoazobenzene and phenol. Indicate chromophores and auxochromes in the obtained azo dyes.

1582. Formulate the main principles of the modern theory of chromaticity of organic compounds.

1583. Why is 1,2-diphenylethylene colourless (λ_{max} = = 319 nm) while 1,10-diphenyl-1,3,5,7,9-decapentaene is orange (λ_{max} = 424 nm)?

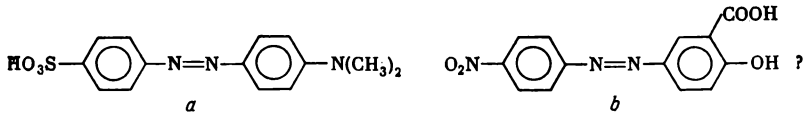
1584. *p*-Nitrophenolate ion gives an intense yellow colour to an aqueous solution (λ_{max} = 400 nm, ε = 15,000). Why

does the colour weaken on acidification (λ_{max} = 320 nm, ε = 9000)?

1585. An aqueous solution of *p*-dimethylaminoazobenzene is bright yellow (λ_{max} = 420 nm), but becomes intense red (λ_{max} = 530 nm) on adding dilute acid. What chemical reaction accounts for the change of colour?

1586*. Using 4-hydroxy-4′-dimethylaminoazobenzene as an example, indicate by what chemical method the structure of the azo dye can be established.

1587. What compounds are formed by the action of stannous chloride (in HCl medium) on the following azo dyes:



1588*. Write the structural formula of the azo dye the reduction splitting of which gives a mixture of *p*-aminophenol and *p*-phenylenediamine.

1589. Write the reaction for preparing methyl orange from benzene. On what properties of this dye does its use as an indicator depend?

D. Establishing the Structure of Organic Compounds by Their Properties

1590. A substance having the composition C_7H_9N is diazotized with subsequent heating of the obtained diazo compound with $Cu_2(CN)_2$, and hydrolysed, to give carboxylic acid, the mononitration of which gives only one isomer. Establish the structure of the compound.

1591*. Establish the structure of the compound $C_7H_8N_2O_2$. It reacts with alkalis to give salts and is diazotized. The diazo compound can be turned into $C_7H_6ClNO_2$ by the Sandmeyer reaction. The latter compound is oxidized into *p*-chlorobenzoic acid.

1592*. Determine the structure of $C_8H_{11}N$ that reacts with strong acids to give salts and with nitrous acid to give $C_8H_{10}N_2O$. The substance does not absorb in the region of 3500-3200 cm^{-1}.

1593*. Establish the structure of the compound $C_7H_8N_2O_2$

having the following properties: (1) it does not react with aqueous sodium hydroxide solution, (2) reacts with mineral acids to give salts, (3) reacts with nitrous acid to turn into an aromatic alcohol the monochlorination of which, in the presence of a catalyst, gives only one isomer.

1594. Establish the structure of the compound $C_7H_{10}N_2$ that reacts with nitrous acid, with subsequent heating, to give *o*-hydroxybenzyl alcohol.

1595*. Determine the structure of the compound $C_6H_5BrN_2O_2$ having the following properties: (1) it is diazotized, (2) when heated with an aqueous solution of sodium hydroxide with subsequent acidification, it easily turns into the compound $C_6H_6N_2O_3$, (3) when reduced with sodium sulphide it turns into bromo-*p*-phenylenediamine.

1596*. Determine the structure of the compound $C_6H_5Br_2NO_3S$ that is diazotized and then heated with alcohol (in the presence of sodium acetate) to give $C_6H_4Br_2O_3S$. The latter is treated with superheated steam in the presence of sulphuric acid to give *m*-dibromobenzene. The compound in question ($C_6H_5Br_2NO_3S$) can be obtained from sulphanilic acid in one step (with a good yield).

1597*. A bright yellow substance having the composition $C_{12}H_{11}N_3$ is heated in the presence of a mineral acid to give an azo dye of the same composition, that can be diazotized. When an aqueous solution of the obtained diazonium salt is heated, *p*-hydroxyazobenzene is formed. Establish the structure of the compound.

1598. Write the structural formula of the compound $C_{14}H_{14}N_2$. It is a pale yellow substance that is acted upon with tin in hydrochloric acid medium to give *p*-toluidine as the only reaction product.

1599*. Write the structural formula of the compound $C_{13}H_{13}N_3$: it is a yellow substance insoluble in water but giving salts with acids. When reduced ($SnCl_2 + HCl$) it gives two products: C_7H_9N and $C_6H_8N_2$. The former product is diazotized and then heated in water to give *o*-cresol, while the latter product is oxidized with chromic-sulphuric acid to give *p*-benzoquinone.

1600*. Establish the structure of the azo dye $C_{12}H_9N_3O_6S$ that is reduced to give sulphanilic acid and $C_6H_6N_2O_3$. Tha latter is desaminated to give *m*-nitrophenol.

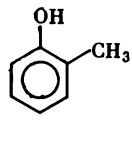
CHAPTER TWENTY-FOUR

PHENOLS. QUINONES. AROMATIC ALCOHOLS

MONOHYDRIC PHENOLS

A. Isomerism. Nomenclature

1601. Name the following compounds:



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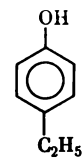

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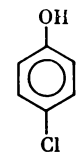

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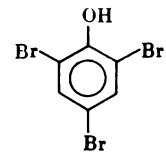

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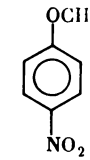

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1602. Write structural formulas of: (a) *m*-cresol, (b) *o*-nitrophenol, (c) phenol-2,4-disulphonic acid, (d) picric acid.

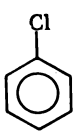
1603. Write structural formulas of all isomers of aromatic compounds having the composition C_7H_8O. Name them.

1604. Give structural formulas of all isomeric xylenols. Name them.

B. Methods of Preparing

1605. Write reactions used for commercial manufacture of phenol: (1) from benzenesulphonic acid, (2) from chlorobenzene, (3) via isopropylbenzene. Explain the mechanisms of the reactions. What is the advantage of the latter method over the others?

1606. Obtain phenols by alkaline hydrolysis of the following compounds:



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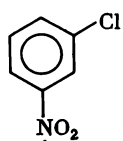

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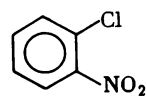

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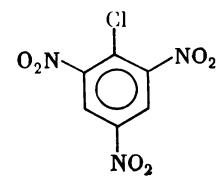

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Specify the reaction conditions. In which compound is the hydroxy group most easily substituted for the chlorine atom? Explain the high reactivity of the chlorine atom.

1607. Obtain: (a) phenol from aniline, (b) *o*-cresol from *o*-toluidine.

C. Properties

1608. Compare the structure of phenol with that of the enol form of cyclohexanone. What is similar and different with them? How can the enol hydroxyl be detected qualitatively in organic compounds?

1609. Which of the following compounds: (a) phenol, (b) benzyl alcohol, (c) *p*-cresol, (d) β-phenylethyl alcohol will give the colour reaction with ferric chloride solution?

1610. Compare the effects that the benzene nucleus produces on the properties of the hydroxyl group in *p*-cresol and in benzyl alcohol. Indicate the most important differences in the chemical properties of these compounds.

1611. What accounts for the acid properties of phenol? Compare the acidity constants of phenol ($pK_a = 10.0$), acetic acid ($pK_a = 4.7$) and carbonic acid ($pK_a = 6.36$). What compound is formed by passing carbon dioxide into an aqueous solution of sodium phenoxide? Write the reaction equation.

1612. What reactions can be used to distinguish between phenol and benzoic acid? How can these compounds be separated?

1613*. Why does 2,4-dinitrophenol ($pK_a = 4.0$) possess stronger acid character than phenol ($pK_a = 10.0$)?

1614. Give the spectral characteristics of phenols. How do the I-R and U-V spectra of benzene differ from those of phenol?

1615. Figure 48 shows the I-R spectra of anisole and *o*-cresol (liquid film). Identify the spectra. Indicate the absorption bands characteristic of separate atom groupings.

1616. Alkylate phenol with: (a) ethyl iodide, (b) dimethyl sulphate, (c) methyl *p*-toluenesulphonate. Give the mechanisms of the O-alkylation reaction.

1617*. By what reagents can phenol be acylated? Explain why it is impossible to obtain phenyl acetate by the reaction of phenol with acetic acid.

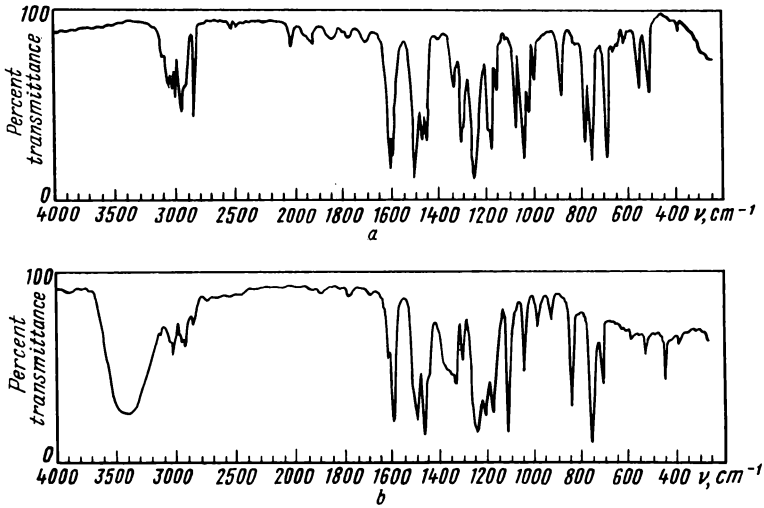


Fig. 48. I-R spectra of anisole and *o*-cresol

1618*. Substitution of bromine for the hydroxyl group by the action of hydrogen bromide is easy in alcohols and practically impossible in phenols. Explain.

1619*. What compounds are formed by heating phenyl acetate with aluminium chloride (1:1)? Write the reactions.

1620. Compare the reactivity of benzene and phenol in electrophilic substitution reactions. Give examples of the reactions and specify their conditions.

1621. Write reactions of phenol with: (a) bromine water, (b) dilute nitric acid, (c) nitrous acid. Characterize the mechanism of electrophilic substitution in phenols.

1622. Suggest a method of synthesizing *o*-bromophenol from phenol (via 2,4-phenoldisulphonic acid).

1623*. Sulphonation of phenol with concentrated sulphuric acid at room temperature gives *o*-phenolsulphonic acid. When the latter is heated to 100°C, the *para*-isomer is formed. How can this conversion be explained?

1624. What compounds are formed by the reaction of phenol with: (1) phenyldiazonium chloride, (2) *p*-tolyldiazonium bisulphate? What medium (acid, alkaline) is required for the reactions?

1625. Consider the mechanism of the reactions of phenol with phenyldiazonium chloride. Compare the reactivity of phenol and phenolate ion in the electrophilic substitution reactions.

1626. Give examples of benzene derivatives that react with nitrous acid to give C-nitroso derivatives. Write the reactions.

1627. What compound will be obtained by hydrogenation of phenol in the presence of a nickel catalyst? What is the commercial importance of this reaction? Compare chemical properties of phenol and its hydrogenation product.

1628. Write the reaction of phenol mononitration. How can a mixture of the formed nitrophenol isomers be separated?

1629*. Suggest a method for preparing *p*-nitrophenol, free from traces of the *ortho*-isomer, from phenol.

1630. Obtain 2,4-dinitrophenol from benzene.

1631. Write the reaction of preparing picric acid from phenol and from chlorobenzene. What method is used for the commercial manufacture of picric acid?

1632*. A nitrating mixture acts on 2,4-phenoldisulphonic acid to ensure a good yield of picric acid. Write the reaction.

1633*. Explain the cause of increasing acid properties in the following series:

phenol	< *m*-nitrophenol	< *p*-nitrophenol
($pK_a = 10.0$)	($pK_a = 8.39$)	($pK_a = 7.15$)

1634. Which of the following compounds: (a) phenol, (b) *p*-nitrophenol, (c) picric acid will react with an aqueous solution of soda? Write the reactions.

1635. Write the reactions of subsequent action on phenol of the following substances: (a) dilute nitric acid, (b) dimethyl sulphate in an alkaline medium, (c) iron in the presence of hydrochloric acid, (d) acetyl chloride. Name the compounds formed in the reactions.

1636. What reactions can be used to distinguish between the following compounds?

$$C_6H_5—O—CH_2—COOH \quad \text{and} \quad p\text{-}C_6H_4\begin{matrix}OH\\COCH_3\end{matrix}$$

1637. Write structural formulas of the intermediate and final products in the following:

$$\text{phenol} \xrightarrow[\text{(Ni, p, heat)}]{3H_2} \ldots \xrightarrow[250°C]{Cu} \ldots \xrightarrow[NaOH]{KMnO_4} \ldots \xrightarrow[H_2O]{HCl} \ldots$$

1638. What compounds are formed by the following conversions?

$$\text{benzene} \xrightarrow[\text{heat}]{H_2SO_4} \ldots \xrightarrow[\text{fusion}]{NaOH} \ldots \xrightarrow{\text{HCl (acid)}}$$

$$\xrightarrow[NaOH]{(CH_3O)_2SO_2} \ldots \xrightarrow[H_2SO_4]{HNO_3} \ldots$$

1639. Fill in the formulas of the formed compounds into the following and name the compounds:

$$C_6H_5OH \xrightarrow[NaOH]{C_2H_5I} \ldots \xrightarrow[H_2SO_4]{HNO_3} \ldots \xrightarrow{Fe+HCl} \ldots$$

$$\ldots \xrightarrow{\text{excess } CH_3I} \ldots \xrightarrow{NaOH} \ldots$$

1640*. Complete the following:

$$p\text{-nitrochlorobenzene} \xrightarrow[\text{heat}]{H_2SO_4 \text{ (fumes)}} \ldots \xrightarrow[H_2SO_4, \text{ heat}]{HNO_3} \ldots$$

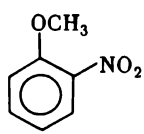
$$\ldots \xrightarrow[H_2O]{NaOH} \ldots \xrightarrow[H_2O]{HCl} \ldots$$

Name the compounds.

1641. Suggest a method of synthesizing phenacetin (*p*-ethoxyacetanilide) from phenol.

1642. Obtain *o*-chlorophenol from *p*-phenolsulphonic acid (using the desulphonation reaction).

1643. Fill in the formulas of the intermediate and end products into the following:



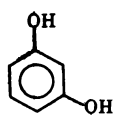
$$\xrightarrow{(Fe+HCl)} \ldots \xrightarrow[0°C]{NaNO_2+2HCl} \ldots \xrightarrow[heat]{HOH} \ldots \xrightarrow[pyridine]{C_6H_5COCl} \ldots$$

Name the compounds.

POLYHYDRIC PHENOLS

A. Isomerism. Nomenclature. Methods of Preparing

1644. Name the following compounds: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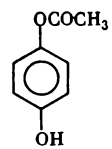
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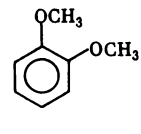
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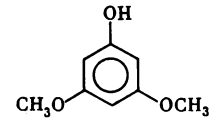
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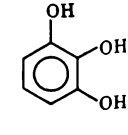
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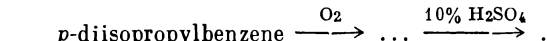
1645. Write structural formulas of all isomers of dihydroxybenzene, trihydroxybenzene, tetrahydroxybenzene. Name them.

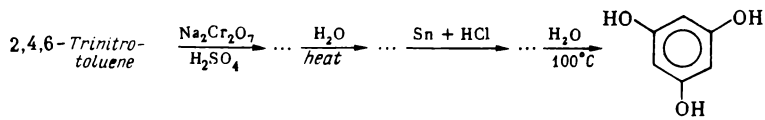
1646. Suggest a method for preparing pyrocatechol, resorcinol, and hydroquinone from benzene.

1647*. Fill in the formulas of the intermediate and end products into the following:



Name the compounds.

1648. Phloroglucinol can be obtained from trinitrotoluene by the following conversions:



Complete the reaction and name all intermediate compounds.

B. Properties

1649. What is the chemical behaviour of *o*- and *p*-dihydroxybenzenes as compared with phenol? Write the corresponding reactions.

1650. What compounds are formed by oxidation of pyrocatechol, of hydroquinone?

1651. What property of pyrogallol is used in quantitative determination of oxygen in gas mixtures?

1652. Characterize di- and trihydric phenols having the hydroxyl groups in the *meta*-position.

1653. Write reactions of phloroglucinol in which it behaves like: (a) trihydric phenol, (b) tricarbonyl compound. How can the specific chemical behaviour of phloroglucinol be explained?

Quinones

1654. Write the reactions of preparing *o*- and *p*-benzoquinones from the corresponding dihydroxybenzenes. What is the commercial method of manufacture of *p*-benzoquinone?

1655. Consider the structure of *p*-benzoquinone. How does the length of the C—C bond depend on the conjugation? What accounts for the easiness with which *p*-benzoquinone is converted into an aromatic compound?

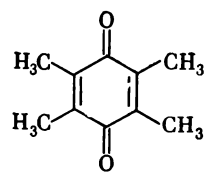
1656. Give the general characteristics of the properties of *p*-benzoquinone.

1657. What reaction can prove the presence of two carbonyl groups in a molecule of quinone?

1658. Write the reaction of quinone reduction with sulphur dioxide. What is the practical use of the reaction product?

1659. Write the reaction of preparing quinhydrone. Write the electrochemical equation on which the use of quinhydrone for determining pH is based.

1660*. Arrange the following quinones in the order of their decreasing redox potential:



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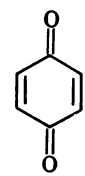

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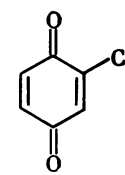

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1661. Write reactions of *p*-benzoquinone with HCl, HCN and $NaHSO_3$. Give the mechanism using the reaction with HCl as an example.

1662. What compounds can be obtained by the action of bromine on quinone?

1663*. Add 1.1 mole of butadiene to a suspension of *p*-benzoquinone in acetic acid at 16°C. A colourless solution forms in 40 hours. Heat the solution with dilute hydrochloric acid: colourless crystals precipitate. What is the resultant compound? Write the reactions.

1664*. The action of hydroxylamine (1 mole) on quinone, and the action of nitrous acid on phenol result in the formation of the same compound. Explain.

1665*. Using methyl orange as an example, explain the concept of the benzoid-quinoid tautomerism.

1666*. Write the reaction of preparing chloranil (2,3,5,6-tetrachloro-1,4-benzoquinone) from phenol. What are the uses of chloranil?

1667. *o*-Chloranil (tetrachloro-1,2-benzoquinone) oxidizes the alcohol group to aldehyde group without producing any effect on the double bond. What is formed by the action of cinnamic alcohol on *o*-chloranil?

AROMATIC ALCOHOLS

1668. Name the following compounds:

(a) $C_6H_5CH_2OH$, (b) $C_6H_5CH_2CH_2OH$, (c) $C_6H_5-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}-OH$

(d) $C_6H_5CH_2-\overset{\displaystyle C_6H_5}{\underset{\displaystyle C_6H_5}{\overset{|}{\underset{|}{C}}}}-OH$, (e) $CH_3-\underset{\displaystyle C_6H_5}{\underset{|}{CH}}-\overset{\displaystyle OH}{\overset{|}{CH}}-CH_3$

1669. Write structural formulas of the following alcohols: (a) diethylphenylcarbinol, (b) ethyl-*o*-tolylcarbinol, (c) isopropylphenylcarbinol, (d) dimethylbenzylcarbinol.

1670. Write the reaction of preparing benzyl alcohol by all known methods.

1671. Use the Grignard reaction to obtain: (a) dimethylphenylcarbinol, (b) dibenzylcarbinol.

1672. Suggest a method to synthesize methylethylbenzylcarbinol from toluene.

1673. What compound will be formed by the following conversions?

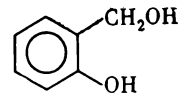
$$C_6H_5Cl \xrightarrow[\text{heat, P}]{Mg} \xrightarrow{CH_2-CH_2 \diagdown O \diagup} \ldots \xrightarrow[H+]{HOH} \ldots$$

1674. What reactions can be used to distinguish between the following isomers: *o*-cresol and benzyl alcohol? Suggest a chemical method for separation of these compounds.

1675. Write the reactions of benzyl alcohol with: (a) sodium, (b) acetic acid (in the presence of sulphuric acid), (c) phosphorus pentachloride. Name the reaction products.

1676. What compounds can be obtained by oxidizing benzyl alcohol?

1677. How can it be proved that saligenol contains one alcohol and one phenol hydroxyl?



1678. By what reactions is it possible to distinguish between the isomers $C_6H_5OCOCH_3$ and $C_6H_5COCH_2OH$?

1679. Give examples of the following compounds: (1) a substituted phenol reacting with soda, (2) a substituted phenol that does not react with HNO_2 nor enter the azo coupling reaction, (3) a dihydric phenol the oxidation of which gives quinone, (4) a trihydric phenol capable of forming both trienol derivatives and triketone derivatives, (5) *p*-quinone having lower oxidation potential than *p*-benzoquinone.

C. Establishing the Structure of Organic Compounds by Their Properties

1680. Write a structural formula of the compound $C_8H_{10}O$ that reacts with alkalis to give salts, is methylated with dimethyl sulphate in an alkaline medium. The oxidation

of the methylation product gives *m*-methoxybenzoic acid.

1681. Write a structural formula of the compound $C_6H_6O_4S$ that reacts with an aqueous solution of alkali to give $C_6H_4O_4SNa_2$. The latter is fused with alkali and acidified to give resorcinol.

1682. The substance C_7H_8O does not give colour reaction with ferric chloride and is oxidized into benzoic acid. Establish the structural formula of the compound.

1683. Write a structural formula of the substance C_7H_7ClO that: (a) reacts with PCl_5 to give $C_7H_6Cl_2$, (b) is oxidized to give *p*-chlorobenzoic acid.

1684*. Write all possible structural formulas of the compound $C_9H_{12}O$ that reacts with alkalis to give salts. The product of its methylation with dimethyl sulphate in an alkaline medium gives, on oxidation, *p*-methoxybenzoic acid.

1685*. Establish the structure of and suggest a method for preparing $C_8H_8O_3$ that reacts with sodium bicarbonate to liberate carbon dioxide, and when heated with concentrated hydrobromic acid gives phenol and bromoacetic acid.

1686*. Establish the structure of styphnic acid, $C_6H_3N_3O_8$, that is obtained by the nitration of *m*-nitrophenol with the subsequent boiling of the reaction product with water.

1687*. Establish the structure of an aromatic compound having the composition C_7H_8O, the I-R spectrum of which does not absorb at 3700-3200 cm^{-1}.

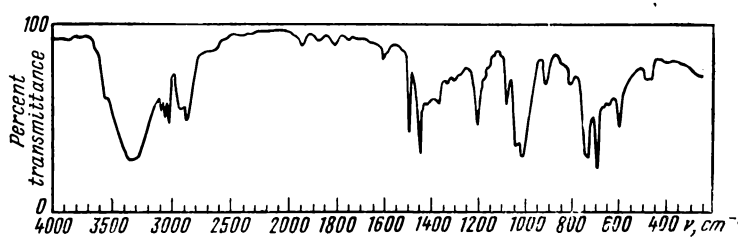


Fig. 49. I-R spectrum of C_7H_8O

1688*. A substance having the formula $C_9H_{12}O$ reacts with alkalis to give salts. Its NMR spectrum has three singlets: δ_1 2.10 ppm, δ_2 4.13 ppm and δ_3 6.60 ppm, the intensities relating as 9:1:2. Establish the structure of the compound.

1689*. Establish the structure of C_7H_8O by its I-R (liquid film) and NMR spectra (Figs. 49 and 50).

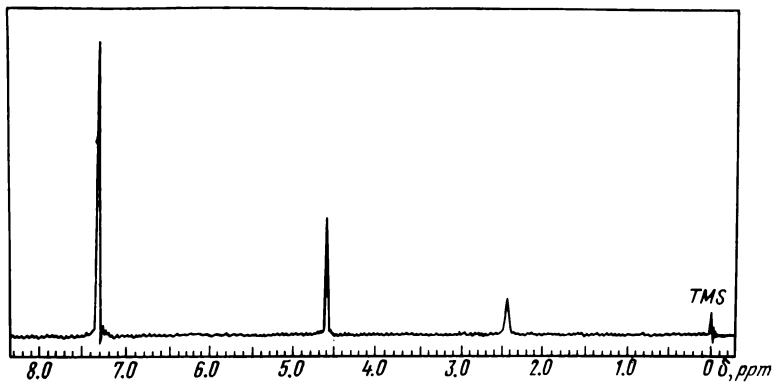


Fig. 50. NMR spectrum of C_7H_8O

1690*. Establish the structure of $C_6H_5NO_2$, having the following properties: (1) it reacts with NH_2OH to give $C_6H_6N_2O_2$, (2) is oxidized to *p*-nitrophenol, (3) is reduced to *p*-aminophenol.

1691*. A yellow crystalline substance, $C_6Cl_4O_2$, was obtained from *p*-phenylenediamine by the action of $KClO_3$ in hydrochloric acid. It is stable to oxidizing agents, but is easily reduced to $C_6H_2Cl_4O_2$. Establish the structure of the compound.

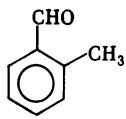
CHAPTER TWENTY-FIVE

AROMATIC ALDEHYDES AND KETONES

A. Isomerism. Nomenclature

1692. Write structural formulas of all isomers of aromatic carbonyl compounds having the composition C_8H_8O, and name them.

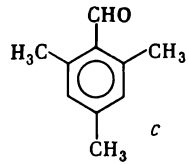
1693. Name the following compounds:



a

$C_6H_5CH_2CHO$

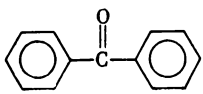
b



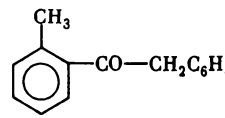
c

$C_6H_5CH{=}CH{-}CHO$

d



e



f

1694. Write structural formulas of the following compounds: (a) α-phenylpropionaldehyde, (b) *o*-nitrobenzaldehyde, (c) ω-chloroacetophenone, (d) *tert*-butylphenyl ketone, (e) 2,6-disulphobenzaldehyde, (f) *p,p'*-di-(dimethylamino)benzophenone.

B. Methods of Preparing Aldehydes

1695. Write the reactions for preparing benzaldehyde by all known methods. Indicate the general and also specific methods for preparing aromatic aldehydes.

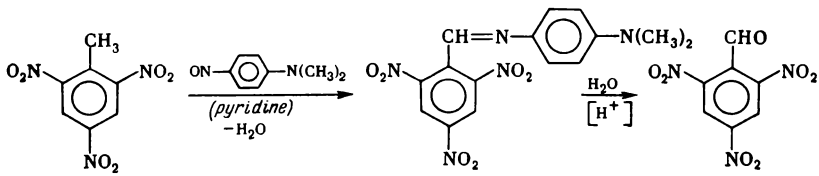
1696. Write reactions for preparing benzaldehyde, *o*-toluic and phenylacetic aldehydes: (a) by oxidation of the corresponding alcohols, (b) by hydrolysis of dihalogen-substituted compounds.

1697. Write the reaction equations for oxidation of: (a) *o*-chlorotoluene to *o*-chlorobenzaldehyde, (b) *m*-xylene

to *m*-toluic aldehyde. What oxidizing agents should be used to oxidize the methyl group to aldehyde group?

1698. Suggest three methods for conversion of toluene into benzaldehyde. What side products can be formed in the reaction?

1699*. 2,4,6-Trinitrobenzaldehyde is obtained as follows:



Can 2,4,6-trimethylbenzaldehyde be prepared by the same method?

1700. What methods can be used to introduce the aldehyde group directly into the aromatic nucleus? What reagents and catalysts are required in each particular case? Give examples.

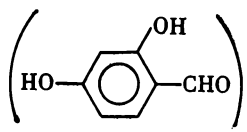
1701*. Write the reactions of toluene and mesitylene formylation with formyl fluoride in the presence of BF_3. Give the reaction mechanisms.

1702. Obtain *p*-isopropylbenzaldehyde and also 2,5-dimethylbenzaldehyde by the Gattermann-Koch reaction.

1703*. Write the reaction of preparing salicylaldehyde by the Reimer-Tiemann reaction. Explain the mechanism of the reaction. What side product is formed? How can it be separated from the main reaction product?

1704. Write the synthesis of vanillin (3-methoxy-4-hydroxybenzaldehyde) from monomethyl ether of pyrocatechol by the Reimer-Tiemann reaction.

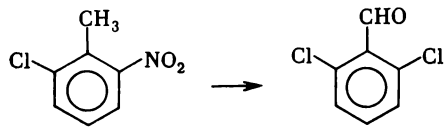
1705. Write the reaction of preparing resorcylaldehyde



from resorcinol by the Gattermann method.

1706. Suggest methods for preparing *p*-methoxybenzaldehyde: (a) from *p*-hydroxybenzaldehyde, (b) from *p*-cresol, (c) from anisole.

1707. Write the following conversion in detail:



1708*. Obtain *m*-hydroxybenzaldehyde from benzaldehyde.

1709*. Obtain 2-hydroxy-5-aminobenzaldehyde from phenol.

1710. Suggest methods for preparing terephthalic aldehyde from *p*-xylene.

1711. Write the synthesis of cinnamaldehyde from acetylene and toluene.

1712. A fragrant substance 'jasmine aldehyde' (alpha-amyl cinnamaldehyde) has the following formula: $C_6H_5-CH=\underset{\displaystyle CHO}{\underset{|}{C}}-CH_2-CH_2-CH_2-CH_2-CH_3$. Write the reaction of its preparation from benzaldehyde and aldehyde $CH_3(CH_2)_5CHO$.

C. Methods of Preparing Ketones

1713. Obtain benzophenone by all known methods. Which of them are general and which are specific methods for preparing aromatic ketones?

1714. Write the reactions of preparing acetophenone: (a) by oxidation of an aromatic hydrocarbon, (b) by oxidation of an alcohol, (c) by hydrolysis of a dihalogen-substituted compound.

1715. Write the Friedel-Crafts reaction for preparing: (a) benzophenone, (b) ω-chloroacetophenone, (c) *p*-bromoacetophenone, (d) butyrophenone. Compare the mechanisms of acylation and alkylation of aromatic compounds by the Friedel-Crafts method.

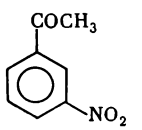
1716*. Methylation of benzene by the Friedel-Crafts reaction, in addition to toluene, gives also polymethylbenzenes, while acetylation in the same conditions gives mainly acetophenone. Explain.

1717. How can it be explained that the relative rates of C-benzoylation of aromatic compounds in the presence of aluminium chloride at 25°C have the following values:

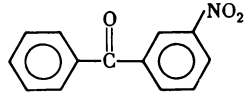
Substance	C_6H_6	$C_6H_5CH_3$	$C_6H_5C(CH_3)_3$	m-$C_6H_4(CH_3)_2$	C_6H_5Cl
k	1	110	140	3940	0.0115

1718. Obtain the following ketones by the Friedel-Crafts reaction: (a) *p*-methylacetophenone, (b) 2,4-dimethylacetophenone, (c) *p*-chloroacetophenone. Which of these ketones is the easiest to obtain?

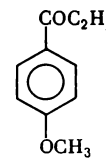
1719*. Can the following ketones be obtained by acylation (or aroylation) of the corresponding aromatic compounds by the Friedel-Crafts method:



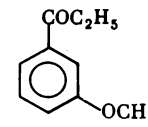
a



b



c



d

Write possible reactions.

1720*. Suggest a method for preparing *m*-nitropropiophenone from benzene.

1721. What ketone is formed by heating phosgene with excess dimethylaniline? Write the reaction.

1722. Write the reaction occurring during heating phenyl acetate with aluminium chloride (Fries rearrangement). Consider the reaction mechanism.

1723. Write the reactions for preparing the following hydroxyketones by the Fries rearrangement: (a) *p*- and *o*-hydroxypropiophenones, (b) 2-methyl-4-hydroxyacetophenone and 4-methyl-2-hydroxyacetophenone. How can the products of the rearrangement be separated chemically from the starting compound?

1724. Use the Grignard reaction to obtain: (a) ethyl phenyl ketone from the nitrile of the corresponding acid, (b) phenyl-*p*-tolyl ketone from the acid chloride.

1725. Obtain dibenzyl ketone from benzene.

D. Properties of Aldehydes

1726. Compare the ability of benzaldehyde and phenylacetaldehyde to enter nucleophilic addition reactions. Give examples. Explain the differences.

1727. Describe qualitative changes occurring in the U-V spectrum of benzene after substitution of the aldehyde group for the hydrogen atom.

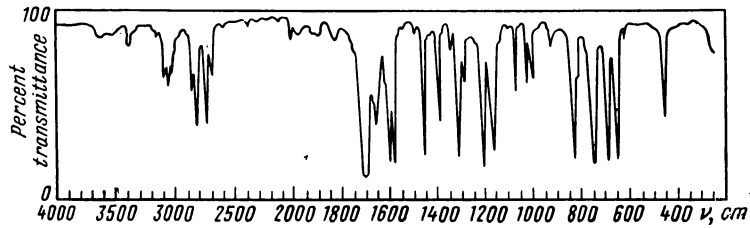


Fig. 51. I-R spectrum of benzaldehyde

1728. Write the reactions that are common for aromatic and fatty aldehydes, using benzaldehyde and propionaldehyde as examples.

1729. By what absorption bands in the I-R spectrum can the presence of the aldehyde group be established in an aromatic compound? Identify as many as possible absorption bands in the I-R spectrum of benzaldehyde (liquid film, Fig. 51).

1730. What compound is formed by oxidation of benzaldehyde with atmospheric oxygen? Write the reaction and consider the mechanism of autooxidation.

1731. How can the aldehyde group be removed from the aromatic nucleus (be replaced by hydrogen)?

1732. Explain which of the following aldehydes will easier enter nucleophilic addition reaction: (a) benzaldehyde, (b) formaldehyde, (c) propionaldehyde.

1733. Write the reactions of *p*-toluic aldehyde with HCN, $NaHSO_3$, C_6H_5MgBr (abs. ether). Will it be easier for *p*-nitrobenzaldehyde to react with these substances? Develop your reasons.

1734. Arrange the following aldehydes in the order of their reactivity in nucleophilic addition reactions: (a) benzaldehyde, (b) 2,4,6-trinitrobenzaldehyde, (c) *p*-dimethylaminobenzaldehyde.

1735. Write the reactions for preparing oxime, hydrazone, and phenylhydrazone of *p*-chlorobenzaldehyde. What is the mechanism of these reactions?

1736. By what reactions can benzaldehyde be distinguished from aliphatic aldehydes?

1737. Suggest the simplest reactions by which the following aldehydes can be differentiated: (a) benzoic and butyric, (b) *p*-toluic and phenylacetic.

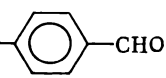
1738. Which of the following aldehydes: (a) formic, (b) acetic, (c) *p*-toluic, (d) phenylacetic, (e) trimethylacetic can enter the Cannizzaro reaction?

1739. Write the Cannizzaro reaction for benzaldehyde. Consider its mechanism.

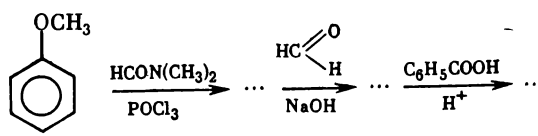
1740*. What reaction is known as the cross Cannizzaro reaction? Write the cross Cannizzaro reaction for formaldehyde and *p*-methoxybenzaldehyde. What is the advantage of this reaction over the ordinary Cannizzaro reaction?

1741*. Why are formic acid and aromatic alcohol predominantly formed in the cross Cannizzaro reaction of benzaldehyde with formaldehyde?

1742*. Write the intramolecular Cannizzaro reactions for the following compounds: (a) $C_6H_5—CO—CHO$,

(b) 

1743*. Accomplish the following conversions:



Name the formed compounds.

1744. Write the reaction of benzoin condensation of benzaldehyde. Consider the reaction mechanism. What are specific characteristics of the catalyst used in the reaction?

1745. What is the structure of benzoins formed from the following mixtures: (a) *p*-toluic and benzoic aldehydes, (b) *p*-methoxybenzaldehyde and *p*-chlorobenzaldehyde?

1746. Can the aldol and croton condensation be accomplished by the action of the following paraldehydes: (a) C_6H_5CHO and p-$CH_3C_6H_4CHO$, (b) C_6H_5CHO and CH_3CH_2CHO, (c) $C_6H_5CH{=}CH{-}CHO$ and $C_6H_5CH_2CHO$, (d) C_6H_5CHO and $(CH_3)_2CH{-}CH{=}CH{-}CHO$? Write the reaction equations and explain them.

1747. How will benzaldehyde react, in the presence of bases, with the following: (a) acetaldehyde, (b) butyraldehyde, (c) methyl ethyl ketone? What is the mechanism of these reactions?

1748. Write the reactions of *p*-toluic aldehyde with: (a) acetic anhydride in the presence of $CH_3COO^-Na^+$ (Perkin reaction), (b) aniline, (c) phenol (two moles).

1749.* Complete the following:

$$C_6H_5CHO \xrightarrow[NaOH]{CH_3NO_2} \ldots \xrightarrow[H_2O]{HCl} \ldots \xrightarrow[-H_2O]{heat} \ldots$$

Write tautomeric forms for the second step product.

1750*. Use benzaldehyde to obtain: (a) β-phenylpropionic acid, (b) β-phenyl-β-aminopropionic acid.

1751. Complete the following

$$C_6H_5Br \xrightarrow[abs.ether]{Mg} \ldots \xrightarrow{CH_3O\text{-}C_6H_4\text{-}CHO} \ldots \xrightarrow[H^+]{H_2O} \ldots$$

1752. Give examples of three aromatic or fatty-aromatic aldehydes having only one of the following properties: (a) enter the aldol and croton condensation, (b) form aldol but do not give products of croton condensation, (c) do not enter the Cannizzaro reaction.

E. Properties of Ketones

1753. Compare the I-R spectrum of benzophenone with its structural formula (liquid film, Fig. 52). Note the characteristic frequencies.

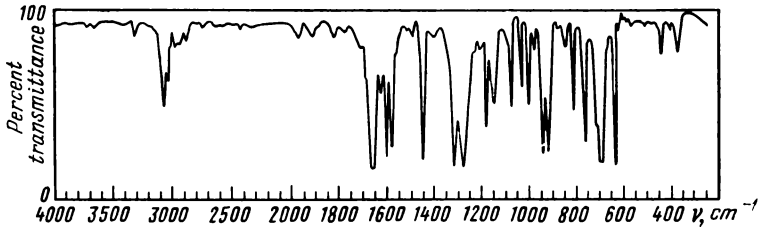


Fig. 52. I-R spectrum of benzophenone

1754. Characterize the U-V spectrum of acetophenone (ethanol, Fig. 53). How does the carbonyl group influence the benzene absorption bands?

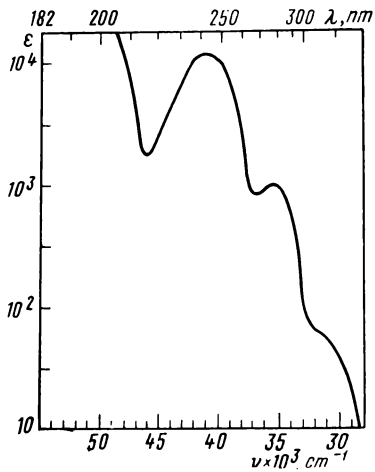


Fig. 53. U-V spectrum of acetophenone

1755. Using practical examples, characterize the different reactivity of the keto group in the molecules of benzophenone and acetone.

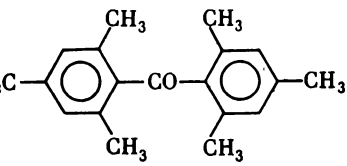
1756. What products are formed by the reduction of propiophenone with: (a) sodium metal in alcohol, (b) amalgamated zinc in hydrochloric acid?

1757. Write the reaction of the formation of benzpinacol from benzophenone.

1758. By what chemical reactions can acetophenone be distinguished from benzaldehyde?

1759. Compare and explain the affinity of the following carbonyl compounds for nucleophilic addition reactions: (a) $C_6H_5COCH_3$ and CH_3COCH_3, (b) $C_6H_5COC_6H_5$ and CH_3COCH_3, (c) $C_6H_5COC_6H_5$ and C_6H_5CHO.

1760. Arrange the following aldehydes and ketones in the order of their increasing reactivity in nucleophilic addition reactions: (a) C_6H_5CHO, (b) $C_6H_5COCH_3$, (c) $C_6H_5COC_6H_5$,

(d) CH_3CHO, (e) 

Indicate the compound in which steric hindrances are of the greatest importance.

1761. Why is hydrocyanic acid added to acetophenone to give the yield of 90 per cent, whereas its addition to phenyl-*tert*-butyl ketone ensures the yield of only 46 per cent?

1762*. Draw formulas of stereoisomers of benzaldehyde oxime. Which of them is the easiest to dehydrate with the formation of a nitrile?

1763. Write the reaction of oximation of phenyl-*p*-tolyl ketone. Draw the configurations of the stereoisomeric oximes. Name them.

1764. Write the Beckmann rearrangement for benzophenone oxime. Consider the reaction mechanism. What catalysts are used in this reaction?

1765. What compounds are formed by the Beckmann rearrangement of stereoisomers of *p*-methoxybenzophenone oxime? What products are formed in their hydrolysis?

1766*. The Beckmann rearrangement of an aromatic

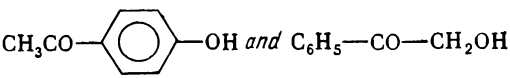
ketone oxime gives N-phenylamide of *p*-ethylbenzoic acid. What is the spatial structure of the starting oxime? Write the structural formula of the corresponding aromatic ketone.

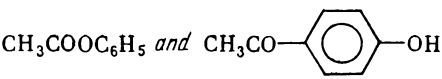
1767. What compounds are formed in hydrolysis of the following products of the Beckmann rearrangement of oximes: (a) anilide of *p*-ethoxybenzoic acid, (b) *p*-ethoxyanilide of benzoic acid? What are the configurations of the starting keto oximes?

1768. What compound is formed in the Beckmann rearrangement of cyclohexanone oxime? Indicate its practical importance.

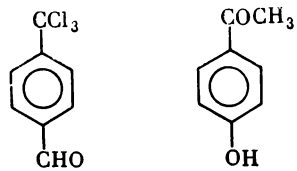
1769. Write the reaction for preparing caprolactam from phenol.

1770. What reactions can be used to distinguish between the following isomers?

(*a*)  *and* $C_6H_5—CO—CH_2OH$

(*b*) $CH_3COOC_6H_5$ *and* 

1771. Write the reactions by which the structure of the following compounds can be proved:



a *b*

1772. Use the Friedel-Crafts reaction to obtain: (a) isopropylbenzene, (b) propylbenzene from benzene.

1773. Write structural formulas of the following aromatic compounds: (a) a ketone that does not form bisulphite derivatives, (b) a ketone substituted in the nucleus that

cannot be obtained by the Friedel-Crafts reaction, (c) a ketone that forms iodoform by the action of iodine in an alkaline medium, (d) a ketone, for whose oxime stereoisomerism is absent, (e) a ketone oxime that undergoes the Beckmann rearrangement to give *p*-methoxyphenylamide of benzoic acid.

F. Establishing the Structure of Organic Compounds by Their Properties

1774. Write the structural formula for C_8H_8O that gives the silver mirror reaction and is oxidized with chromic-sulphuric acid to give benzoic acid.

1775. Determine the structure of the substance $C_7H_4ClNO_3$ that: (a) forms an oxime and phenylhydrazone, (b) is oxidized into 3-chloro-4-nitrobenzoic acid.

1776. The substance C_8H_8O has the following properties: (1) it gives derivatives with NH_2OH and $C_6H_5NHNH_2$, (2) reacts with iodine in an alkaline medium to give iodoform. Write the structural formula of C_8H_8O.

1777*. Establish the structure of C_8H_7BrO from the following: (1) its I-R spectrum has a strong absorption band at 1685 cm^{-1}, (2) when oxidized with chromic-sulphuric acid it gives *p*-bromobenzoic acid.

1778*. The substance $C_{10}H_{10}O$ is not an aldehyde, but its U-V spectrum is practically the same as of cinnamaldehyde. What conclusion concerning its structure can be drawn?

1779. Establish the structure of an aromatic compound that is oximated and then reduced to β-phenylethylamine.

1780. The substance $C_{14}H_{10}O_2$ reacts with excess hydroxylamine to give dioxime, and is oxidized to give only one product, benzoic acid. Establish the structure of the compound.

1781*. Write the structural formula of the substance $C_{14}H_{12}O_2$ having the following properties: (a) it reacts with NH_2OH to give an oxime, (b) reacts with $C_6H_5NHNH_2$ to give phenylhydrazone, and with its excess it gives phenylos-

azone, (c) is reduced with sodium borohydride to give $C_{14}H_{14}O_2$ that is oxidized with periodic acid to benzaldehyde.

1782*. Establish the structure of the benzene derivative C_7H_5ClO by its NMR spectrum (Fig. 54).

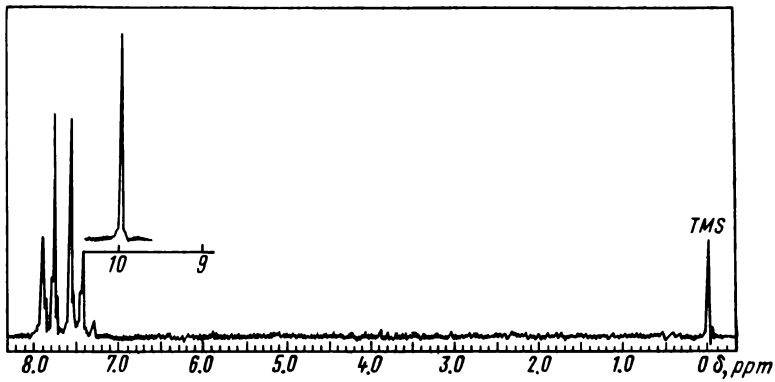


Fig. 54. NMR spectrum of C_7H_5ClO

CHAPTER TWENTY-SIX

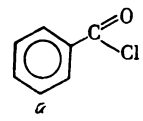
AROMATIC CARBOXYLIC ACIDS

A. Isomerism. Nomenclature

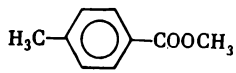
1783. Write the structural formulas of the following: (a) benzoic acid, (b) isomers of toluic acid, (c) isomers of phthalic acid, (d) phenylacetic acid, (e) cinnamic acid.

1784. Write the structural formulas of the following substituted carboxylic acids: (a) salicylic acid, (b) anthranilic acid, (c) isomers of nitrobenzoic acid, (d) *p*-methoxybenzoic acid, (e) gallic acid.

1785. Name the following derivatives of carboxylic acids:



a



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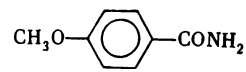

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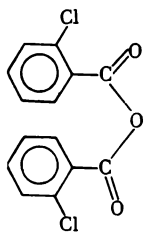

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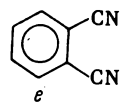

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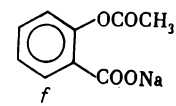

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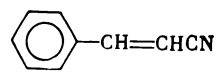


g

1786. Write the structural formulas of all isomers of aromatic acids having the composition $C_8H_8O_2$ and name them.

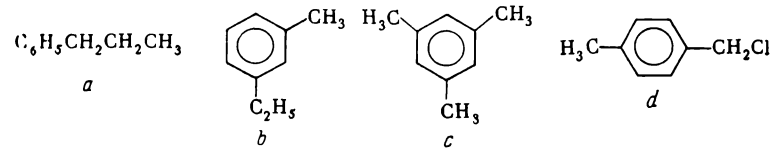
B. Methods of Preparing

1787. Write the reactions for all known methods of preparing benzoic acid. Indicate the specific methods of preparing aromatic acids.

1788. Write the balanced reaction of toluene oxidation with potassium permanganate in an aqueous medium. Cal-

culate the number of grams of the oxidant required theoretically to convert 10 g of toluene into benzoic acid.

1789. What carboxylic acids can be formed by oxidation of the following compounds:



1790. Write the reaction of oxidation with sodium hypochlorite of (a) acetophenone, (b) *p*-methylacetophenone.

1791. Name commercial methods of preparing phthalic acid. Write the reactions.

1792. What methyl aryl ketones are oxidized with sodium hypobromite to give the following: (a) *p*-methoxybenzoic acid, (b) *p*-bromobenzoic acid, (c) *m*-toluic acid?

1793*. Suggest methods for preparing 2,4- and 2,5-dimethylbenzoic acids from *m*- and *p*-xylenes respectively.

1794*. Obtain 1,2,4,5-benzenetetracarboxylic acid: (a) from 1,2,4,5-tetramethylbenzene, (b) from 1,2,4-trimethylbenzene (pseudo-cumene) using the Friedel-Crafts reaction of acylation at one of the stages, (c) from *m*-xylene using the chloromethylation reaction.

1795. Suggest all possible methods of synthesizing benzoic acid from toluene. Indicate commercial methods of manufacture of benzoic acid.

1796. Write the reaction of preparing *o*-toluic and phenylacetic acids by saponification of their nitriles. Indicate methods for preparing nitriles of these acids.

1797. Obtain *p*-toluic acid from: (a) *p*-toluenesulphonic acid, (b) *p*-toluidine.

1798. Write the structural formulas of the intermediate and end products in the following conversions:

(a) $C_6H_6 + COCl_2 \xrightarrow{AlCl_3} \ldots \xrightarrow{H_2O} \ldots$

(b) $C_6H_5CH_3 + COCl_2 \xrightarrow{AlCl_3} \ldots \xrightarrow{H_2O} \ldots$

1799. Use the Cannizzaro reaction to obtain: (a) benzoic acid, (b) 2-iodo-3-hydroxybenzoic acid.

1800. Use the Grignard reaction to obtain: (a) benzoic acid, (b) *p*-toluic acid, (c) phenylacetic acid.

1801. Write the reactions used for commercial manufacture of benzoic acid from naphthalene and from toluene.

1802. Obtain cinnamic acid by the Perkin reaction. Consider the mechanism of the reaction. What is common with the mechanisms of the Perkin reaction and the aldol condensation in the conditions of alkaline catalysis?

1803. Write the formulas of the compounds that are formed by the following reactions:

(a) $C_6H_5CHO + (CH_3CO)_2O \xrightarrow[\text{heat}]{CH_3COONa} \ldots$

(b) $C_6H_5CHO + (CH_3CH_2CO)_2O \xrightarrow[\text{heat}]{CH_3COONa} \ldots$

1804. Suggest a method of synthesizing *o*-bromocinnamic acid from *o*-bromotoluene.

1805*. Suggest a method for preparing δ-phenylvaleric acid from benzaldehyde, acetaldehyde, and acetic anhydride using the Perkin reaction at one of the stages.

1806*. Write the reaction used for commercial manufacture of cinnamic acid from benzylideneacetone.

1807. Write the reaction (and consider its mechanism) for preparing salicylic acid by the Kolbe-Schmidt method. Why does the reaction fail with free phenol?

1808*. What phenols should be used to prepare the following acids by the Kolbe-Schmidt method: (a) 2,4-dihydroxybenzoic, (b) 2,5-dihydroxyterephthalic, (c) *p*-aminosalicylic? Write the balanced reactions.

1809. Obtain all isomers of nitrobenzoic acid from toluene.

1810. Write the reaction for preparing anthranilic acid from phthalimide. Describe the mechanism of the Hofmann rearrangement of amides.

1811. Obtain *o*-chloro- and *o*-iodobenzoic acids: (a) from anthranilic acid, (b) from the corresponding *o*-halogentoluenes.

1812*. Write the conversion of toluene into the following compounds: (a) *p*-aminobenzoic acid, (b) *m*-aminobenzoic acid, (c) β-(*p*-bromophenyl)propionic acid.

C. Properties

1813. Characterize the electronic and spatial structure of a molecule of benzoic acid. Compare the acid properties of benzoic and acetic acids.

1814. Explain in which of the following compounds the acid properties are stronger than in benzoic acid: (a) propionic acid, (b) phenol, (c) *p*-nitrobenzoic acid.

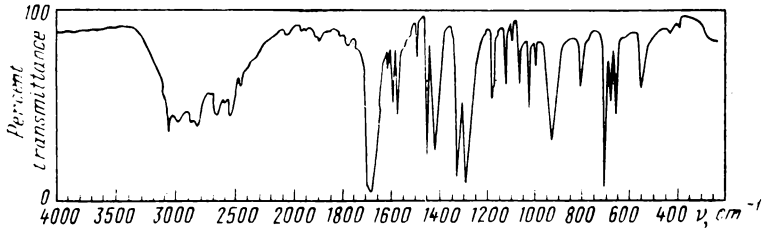


Fig. 55. I-R spectrum of benzoic acid

1815. Write the reaction for preparing benzoic acid and benzyl alcohol from benzaldehyde by the Cannizzaro reaction and suggest your method for the isolation of the reaction products.

1816. Consider the I-R spectrum of benzoic acid (KBr plate, Fig. 55). Indicate characteristic frequencies that are due to the presence of the carboxyl group and the benzene ring.

1817. Bearing in mind the electronic effects of the nucleus substitutes, explain the different acid properties (pK_a at 25°C) of the following substituted benzoic acids:

Substitute	H	NO_2	OH	F
meta-	4.18	3.45	4.08	3.87
para-	4.18	3.43	4.58	4.14

1818. Write the Hammett equation and explain the meaning of each of its terms. What do σ- and ρ-constants characterize? On what do their magnitude and sign depend? How can they be determined?

1819. Describe the Hammett equation for the ionization of *meta-* and *para*-substituted benzoic acids. Use the data given in Problem 1817 to determine σ_{meta} and σ_{para} for the following substitutes: (a) fluorine, (b) hydroxyl group, (c) nitro group.

1820. Characterize the importance and the field of application of the Hammett correlation equation.

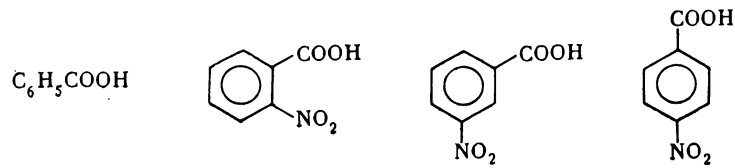
1821. What is known as the *ortho*-effect? Why do *ortho*-substituted benzoic acids, irrespective of the character of the substitute, have a stronger acid character than benzoic acid?

1822. How can the increase in the acid properties of *o*-hydroxybenzoic acid ($pK_a = 3.00$) and *o*-methoxybenzoic acid ($pK_a = 4.09$), compared with the non-substituted benzoic acid ($pK_a = 4.18$) be explained?

1823. What effect does the *ortho*-substitute produce on the acid properties of the following acids: (a) *o*-nitrobenzoic, (b) salicylic, (c) anthranilic?

1824. On what factors does the acidity constant of each isomer of nitrobenzoic acid depend?

Arrange the following compounds in the order of their increasing acid properties:



a *b* *c* *d*

1825. Write reactions for preparing derivatives of benzoic acid: (a) benzoyl chloride (three methods), (b) anhydride (two methods), (c) benzamide, (d) N-phenylamide, (e) benzylbenzoate (two methods), (f) benzonitrile (two methods).

1826*. What conversion has *p*-toluic acid undergone, if the reaction product has the I-R spectrum shown in Fig. 56 (KBr plate)?

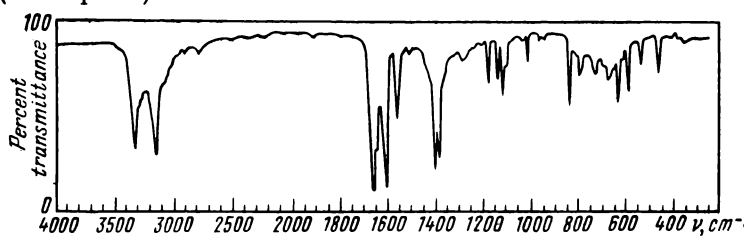
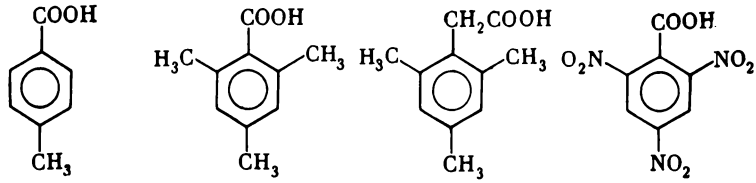


Fig. 56. I-R spectrum of conversion product of *p*-toluic acid

1827. Explain which of the following acids:



a *b* *c* *d*

(a) easily enter the reaction of esterification, (b) form esters with difficulty.

1828. Write the mechanism of benzoic acid esterification with methyl alcohol. Explain which of the acids: benzoic or 2,6-dimethylbenzoic, is easier to be esterified?

1829*. Why is the esterification of 2,6-difluorobenzoic acid with methyl alcohol very difficult to accomplish, while the ester is easy to form by methylation of its silver salt with methyl iodide?

1830*. Why is mesitylenecarboxylic acid difficult to esterify, whereas mesityleneacetic acid esterifies readily?

1831. Use the re-esterification method to obtain: (a) benzyl benzoate from ethyl benzoate, (b) benzyl salicylate from methyl salicylate.

1832*. Compare the acylating power of benzoyl chloride and acetyl chloride. Explain the differences.

1833. Write the reaction of benzoylation of the following compounds: (a) phenol, (b) aniline, (c) benzyl alcohol, (d) anthranilic acid. Characterize the Schotten-Baumann reaction.

1834. Write the reactions and specify their conditions: (a) N-benzoylation of aniline, (b) O-benzoylation of phenol, (c) C-benzoylation of toluene. To what class of compounds do the obtained products belong?

1835. Accomplish the following conversions:

$$2C_6H_5COCl \xrightarrow[0^\circ]{Na_2O_2} \ldots \xrightarrow[0^\circ]{CH_3ONa} \ldots \xrightarrow[0^\circ]{H_2SO_4} \ldots$$

Name all the compounds formed.

1836. By the action of what reagents can the following conversions be accomplished:

$$(C_6H_5CO_2)_2 \xrightarrow{?} C_6H_5CO_3Na \xrightarrow{?} C_6H_5CO_3H \xrightarrow{?}$$

$$\xrightarrow{?} C_6H_5-\underset{\diagdown\,O\,\diagup}{CH}-CH_2 + C_6H_5COOH$$

Name all the compounds.

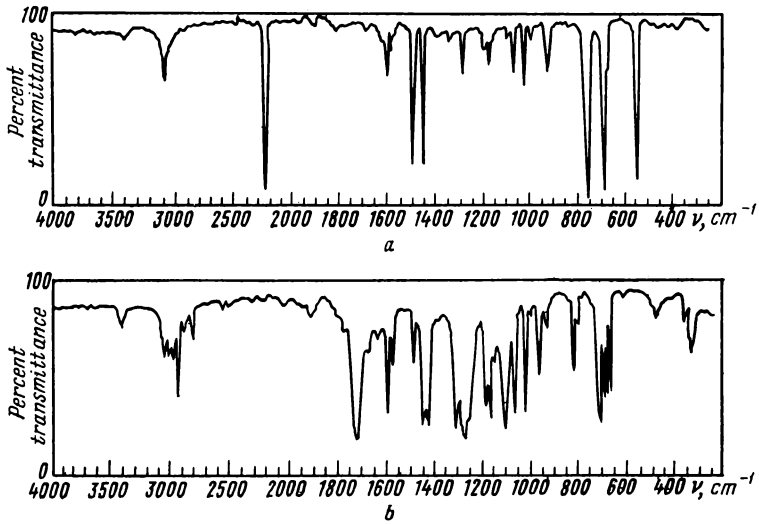


Fig. 57. I-R spectra of methyl benzoate (*a*) and benzonitrile (*b*)

1837. Accomplish the following conversions:

(a) $C_6H_6 \longrightarrow C_6H_5CONH_2$

(b) $C_6H_5CH_3 \longrightarrow C_6H_5CH_2COOH$

(c) $C_6H_5NH_2 \longrightarrow C_6H_5CN$

(d) $C_6H_5CH_3 \longrightarrow C_6H_5COOC_2H_5$

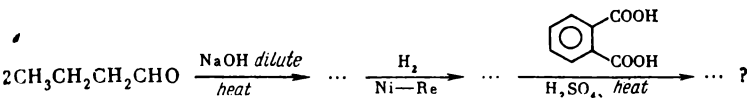
1838. Figure 57 shows I-R spectra of methyl benzoate and benzonitrile (liquid film). Identify the spectra. Indicate characteristic frequencies of the ester and nitrile groups.

1839. Specify the conditions for decarboxylation of (a) benzoic acid, (b) gallic acid. Write the reactions.

1840. Characterize the orienting effect of the carboxyl group in the electrophilic substitution in the aromatic ring. Give examples.

1841. By what chemical reactions can the mixtures of the following compounds be separated: (a) acetophenone and phthalic acid, (b) benzoic acid and benzaldehyde, (c) benzoic acid and phenol, (d) *p*-toluic acid, *p*-toluic aldehyde, and *p*-methylbenzyl alcohol?

1842. What is the structure of the plasticizer dioctyl phthalate, which is manufactured on a commercial scale as follows:



1843. Write the structural formulas of all isomers of phthalic acid. Which of them easily gives the anhydride on heating?

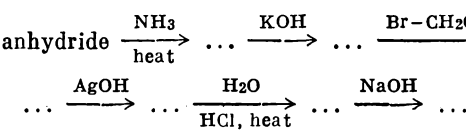
1844. Obtain phthalimide from naphthalene. What accounts for the acid character of this compound?

1845. Write the synthesis of N-ethylphthalimide from *o*-xylene.

1846. Obtain propylamine by the Gabriel reaction. What is the advantage of the Gabriel method of preparing primary amines over the method consisting in alkylation of ammonia?

1847. Write the reactions by which phthalic anhydride is converted into the following compounds: (a) *o*-phthalic acid, (b) phthalimide, (c) anthranilic acid, (d) phenolphthalein, (e) ethyl benzoate.

1848*. Accomplish the following conversions and name the compounds formed in the reactions:



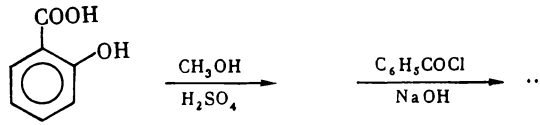
1849. What is the practical importance of the polyester that is formed by re-esterification of dimethyl terephthalate with ethylene glycol? Write the reaction.

1850*. Explain why the acid properties of cinnamic acid are stronger in the *cis-* than in the *trans*-isomer?

1851. Use cinnamic acid to obtain: (a) styrene, (b) ω-bromostyrene.

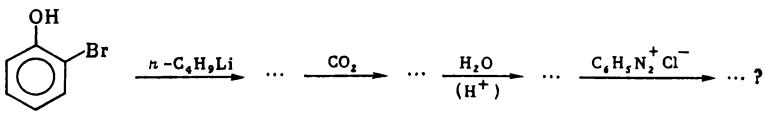
1852. Write the reactions of salicylic acid: (a) with aqueous solution of alkali, (b) acetylation, (c) esterification with ethyl alcohol, (d) decarboxylation, (e) nitration.

1853. Fill in the missing formulas of the intermediate and end products in the following:



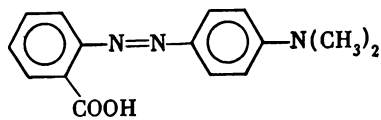
1854. Write the synthesis of ethyl salicylate from benzene.

1855. What compound is formed by the following conversion:



1856. Write the balanced reactions of anthranilic acid that characterize it as an amphoteric compound. Write also the reaction of esterification with methyl alcohol and diazotization in hydrochloric acid medium.

1857. What monoazo- and diazo-components should be used to prepare an azo dye having the following structure:



1858. What derivatives of salicylic acid and *p*-aminobenzoic acid are used in medicine? Write the reactions by which they are prepared.

1859. How can the following groups be introduced in the aromatic nucleus:

—Cl, —OH, —NO_2, —NH_2, —$COCH_3$, —CHO, —COOH?

1860. How can the following groups be removed from (be replaced by hydrogen in) the aromatic nucleus:

Cl, —OH, $-NO_2$, $-NH_2$, $-COCH_3$, —CHO, —COOH?

D. Establishing the Structure of Organic Compounds by Their Properties

1861. Write the structural formula of the compound $C_7H_4Cl_2O$, that is hydrolysed to give *o*-chlorobenzoic acid.

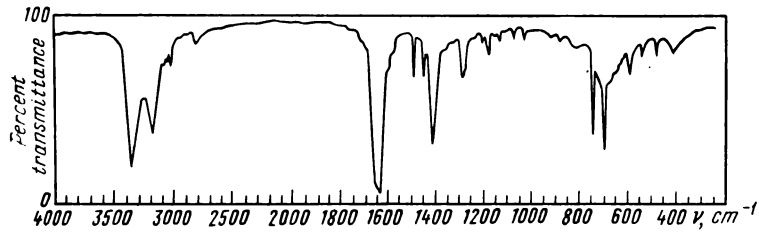


Fig. 58. I-R spectrum of C_8H_9NO

1862*. The substance $C_8H_8O_3$ can be separated into enantiomers; its energetic oxidation gives benzoic acid. Write the structural formula of the compound.

1863*. The compound C_8H_9NO, whose I-R spectrum is shown in Fig. 58 (KBr plate), has the following properties: (a) when heated in an aqueous solution of alkali it liberates ammonia; (b) when reduced with $LiAlH_4$ it gives β-phenylethylamine. Establish the structure of the compound.

1864. Establish the structure of the aromatic compound $C_8H_4O_3$ having the following properties: (a) it reacts with alkalis with heating to give salts, (b) as ammonia is passed into the molten product, phthalimide is formed.

1865*. Establish the structure of the substance $C_7H_6N_2O_3$ that liberates ammonia on heating with dilute alkalis. When the product of its hydrolysis is reduced, anthranilic acid is formed.

1866*. Establish the structure of the compound $C_7H_5BrO_2$ having the following properties: (a) it reacts with alkalis to give salts, (b) it does not give a colour reaction with

ferric chloride, (c) when nitrated it gives one mononitro derivative. Suggest a method for preparing $C_7H_5BrO_2$ from toluene.

1867*. Establish the structure of the compound $C_{10}H_{10}O_2$, whose I-R spectrum is given in Fig. 59 (KBr plate). It has

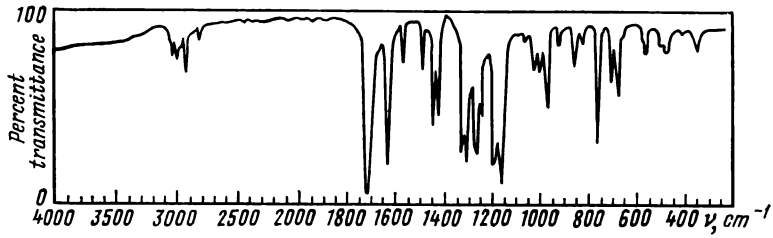


Fig. 59. I-R spectrum of $C_{10}H_{10}O_2$

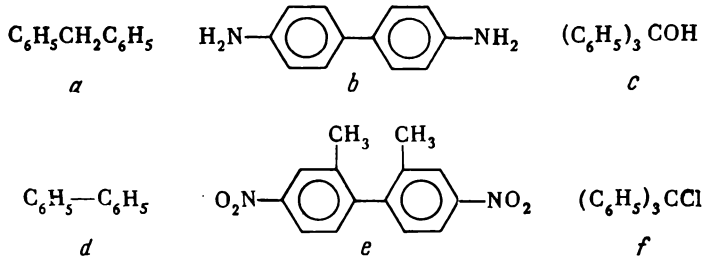
the following properties: (1) decolourizes bromine water, (2) on hydrolysis it gives $C_9H_8O_2$ that reacts with aqueous soda to liberate carbon dioxide, (3) when acidified with potassium permanganate in an acid medium it is converted into benzoic acid.

CHAPTER TWENTY-SEVEN

POLYNUCLEAR AROMATIC COMPOUNDS

COMPOUNDS BELONGING TO THE DIPHENYL, DIPHENYLMETHANE, TRIPHENYLMETHANE GROUP. STABLE FREE RADICALS

1868. Name the following compounds



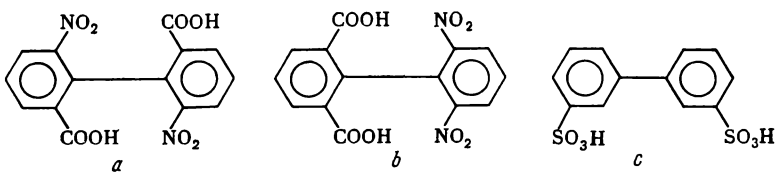
1869. Write the structural formulas of the following compounds: (a) tetraphenylmethane, (b) diphenyl-*p*-tolylcarbinol, (c) 2-methyl-4-nitrodiphenyl, (d) 4,4′-bis-dimethylaminodiphenyl.

1870. Write the structural formulas of all isomers of methyldiphenyl. Name them.

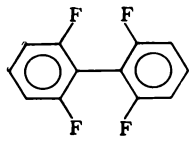
1871. Obtain diphenyl from: (a) benzene, (b) bromobenzene, (c) aniline.

1872. What is the electronic and geometric structure of a diphenyl molecule? Compare its conjugation energy with that of benzene. Characterize the chemical properties of diphenyl.

1873*. What specific characteristics of the structure of diphenyl derivatives account for the appearance in them of optical isomerism (atropoisomerism)? Indicate which of the compounds given below can exist in the form of enantiomers:



1874*. Which of the compounds given below can be split into enantiomers?



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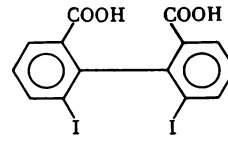

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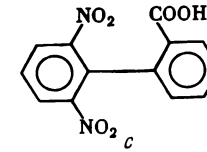

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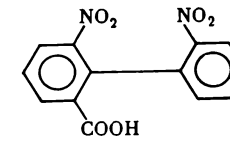
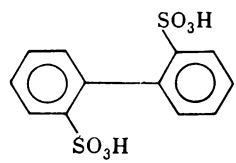
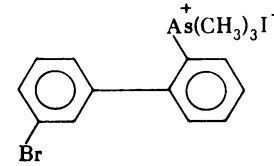


d

1875*. Explain the reasons of appearance of optical isomers in the following diphenyl derivatives:



a



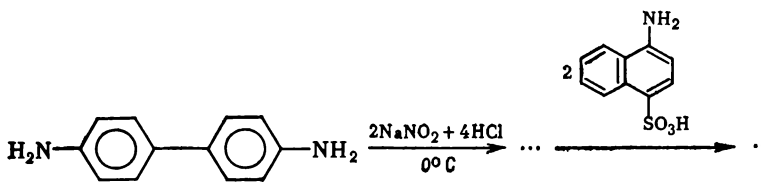
b

1876. Suggest a method for preparing 4,4′-dinitrodiphenyl from benzene.

1877. Write the reaction of preparing benzidine from benzene.

1878. What diphenyl derivative is formed in the benzidine rearrangement of *o*,*o*′-diethylhydrazobenzene?

1879. Complete the following:



1880*. Obtain sym-triphenylbenzene from acetophenone.

1881. Write the reaction of preparing diphenylmethane and triphenylmethane: (a) by the Friedel-Crafts reaction, (b) by condensation of aldehydes with aromatic hydrocarbons.

1882. What compounds can be formed by oxidation of diphenylmethane? triphenylmethane?

1883. Use the Grignard reaction to obtain diphenyl-*p*-tolylcarbinol and di-*o*-tolylcarbinol.

1884. Obtain triphenylcarbinol: (a) from CCl_4 and benzene, (b) from benzophenone. Give the mechanism of the latter reaction.

1885*. What are specific chemical properties of triarylcarbinols? Write the reaction of triphenylcarbinol with concentrated sulphuric acid. What is the motive force of the reaction?

1886*. Why are solutions of triphenylchloromethane in liquid SO_2 bright yellow and conduct electricity?

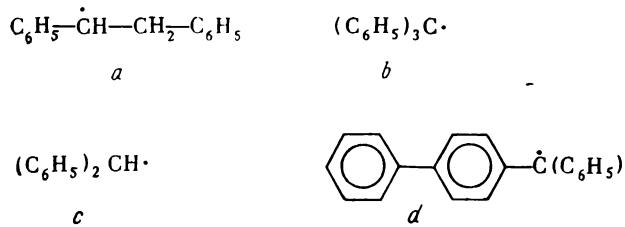
1887*. Why does a colourless ether solution of triphenylmethane turn red as sodium amide is added?

1888. Write the reactions that occur by the action of silver on a benzene solution of triphenylchloromethane: (a) in the absence of air oxygen, (b) in the presence of air oxygen.

1889. Explain the following phenomenon: as zinc acts on a benzene solution of triphenylchloromethane, it turns yellow; on shaking the solution in the air, it is decolourized; the yellow colour re-appears on standing. Write the balanced reactions that occur in the described processes.

1890. Characterize the structure and properties of the triphenylmethyl radical. Why is it stable? What physical method is used in the study of free radicals?

1891. Arrange the following free radicals in the order of their increasing stability:



a *b* *c* *d*

Develop your reasons.

1892. Write the reaction of preparing triphenylmethane dye from benzaldehyde and dimethylaniline. What accounts for its colour?

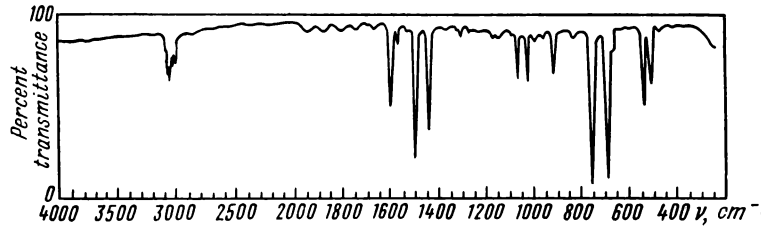
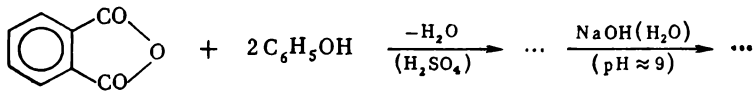


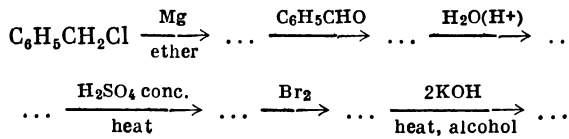
Fig. 60. I-R spectrum of the end product of benzyl chloride conversions

1893. Fill in structural formulas of the intermediate and end products in the following:



On what does the colour of the obtained product depend?

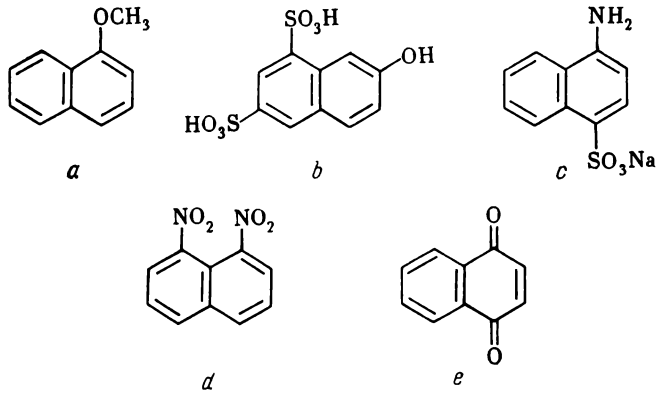
1894*. Accomplish the following conversions:



Compare the structure of the end product with its I-R spectrum (liquid film, Fig. 60).

Compounds with Condensed Benzene Nuclei. Naphthalene Group

1895. Name the following naphthalene derivatives:



a *b* *c* *d* *e*

1896. Write the structural formulas of 1,8-dibromonaphthalene, α-naphthyldiazonium chloride, β-naphthalenecarboxylic acid, decahydronaphthalene.

1897. Write the structural formulas of all isomers of dihydroxynaphthalene.

1898. By what reactions was the structural formula of naphthalene established? Describe the modern view on the structure of a naphthalene molecule.

1899. Compare the aromatic character of naphthalene with that of benzene.

1900. Consider the I-R spectrum of 2-methylnaphthalene (liquid film, Fig. 61). Indicate characteristic frequencies.

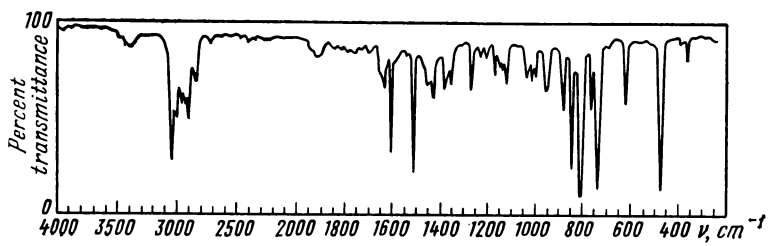


Fig. 61. I-R spectrum of 2-methylnaphthalene

1901. Write the reaction of naphthalene mononitration. Specify the reaction conditions and consider its mechanism. Why is the alpha-position more likely to be involved in the reaction of electrophilic substitution of naphthalene than the beta-position?

1902*. What chemical conversion has naphthalene undergone if the I-R spectrum of the obtained compound has intense absorption bands at 1515 and 1330 cm^{-1}?

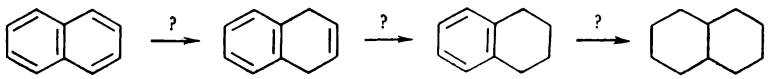
1903. Write the following reactions: (a) chlorination of α-bromonaphthalene, (b) nitration of β-naphthol, (c) sulphonation of α- and β-nitronaphthalenes. Formulate the rule of orientation in the naphthalene nucleus.

1904. What compounds can be obtained by monosulphonation of naphthalene? What is the practical importance of this reaction? Give the mechanism of naphthalene sulphonation.

1905*. Mononitration of naphthalene gives predominantly α-nitronaphthalene, while sulphonation of naphthalene can give (depending on the reaction conditions) either α- or β-naphthalenesulphonic acids. Explain the phenomenon. What are the kinetic and thermodynamic factors of the reaction?

1906. Compare and explain the different activity of naphthalene and benzene in addition reactions.

1907*. By the action of what reagents can the following conversions be effected:



Which of these stages is the most difficult to accomplish and why?

1908. What compounds can be obtained by oxidation of naphthalene? Write the reactions.

1909*. Write the reaction of naphthalene ozonolysis.

1910. Describe the methods used in the commercial manufacture of α- and β-naphthols.

1911. Compare the chemical properties of α-naphthol and α-decalol. Suggest a chemical method of their separation.

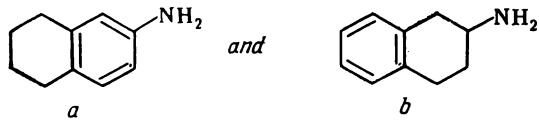
1912. Write the reaction for preparing methyl ether of β-naphthol from naphthalene.

1913. Obtain α- and β-naphthylamines from naphthalene. Write the reactions and specify their conditions.

1914. Use naphthalene to obtain: (a) β-bromonaphthalene, (b) β-nitronaphthalene.

1915. Write the reactions of α-naphthylamine with: (a) HCl, (b) C_2H_5I, (c) CH_3COCl, (d) $NaNO_2$ in the presence of hydrochloric acid.

1916. By what reactions can the following isomers be distinguished?



a *b*

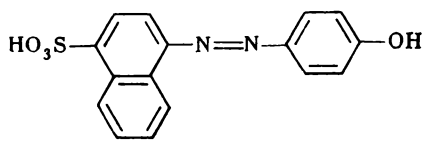
1917. Write the reaction of preparing naphthionic acid from naphthalene.

1918. Obtain 1-naphthol-4-sulphonic acid from naphthalene.

1919. Obtain 1-bromo-2-naphthol from naphthalene.

1920. Write the reactions of preparing azo dyes from the following compounds: (a) α-naphthylamine and β-naphthol, (b) *p*-nitroaniline and α-naphthol.

1921. Use benzene and naphthalene to obtain the azo dye



1922. Use naphthalene to obtain α-naphthalenecarboxylic acid.

1923. Obtain β-naphthalenecarboxylic acid: (a) by oxidation of β-methylnaphthalene, (b) by the action of chlorine

and alkali on methyl-β-naphthylketone. Which of these methods is more effective?

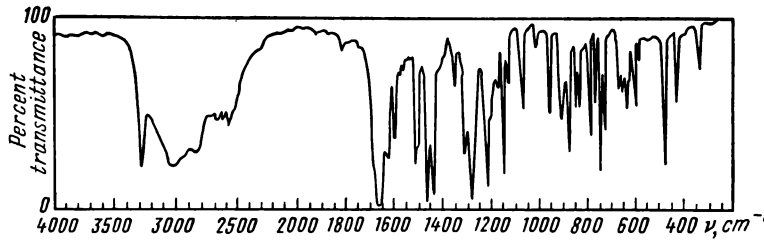
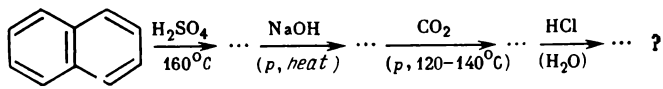


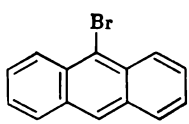
Fig. 62. I-R spectrum of the end product of naphthalene conversions

1924*. What compound has the I-R spectrum shown in Fig. 62 (KBr plate), if the compound is the result of the following conversions:

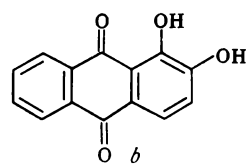


ANTHRACENE GROUP. PHENANTHRENE

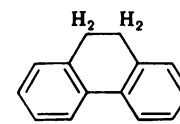
1925. Name the following compounds:



a



b



c

1926. Write the structural formulas of anthraquinone, β-hydroxyanthraquinone, 9-methylphenanthrene, *meso*-bromoanthracene.

1927. Write the structural formulas of all isomers of methylanthracene and methylphenanthrene. Name them.

1928. What is the structure of anthracene and phenanthrene? How do their aromatic properties compare?

1929. Obtain anthracene from *o*-bromobenzyl bromide by the Würtz-Fittig reaction.

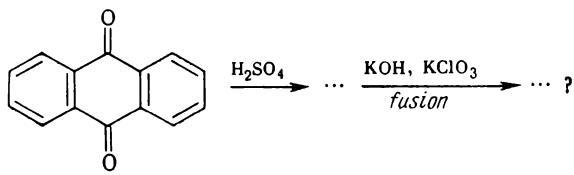
1930. Compare the unsaturated character of anthracene and phenanthrene. Which of these compounds will react with maleic anhydride?

1931. Write the reactions of oxidation of anthracene and phenanthrene to the corresponding quinones. On what does the high activity of the *meso*-positions of anthracene and 9,10-positions of phenanthrene depend?

1932. Obtain anthraquinone from: (a) anthracene, (b) phthalic anhydride.

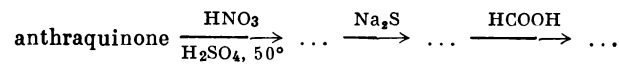
1933. How is sulphonation of anthraquinone effected: (a) without catalysts, (b) with $HgSO_4$ as catalyst?

1934. What compound will be obtained by the following conversions:



What are practical uses of the obtained substance?

1935*. Complete the following:



Name all the compounds.

Establishing the Structure of Organic Compounds by Their Properties

1936. What is the structure of the hydrocarbon $C_{14}H_{14}$, the oxidation of which with chromic-sulphuric acid gives only benzoic acid?

1937*. Establish the structure of the compound $C_{13}H_{12}O$, whose I-R spectrum is shown in Fig. 63 (liquid film). The substance does not form salts with aqueous solutions of alkalis, and easily oxidizes to $C_{13}H_{10}O$.

1938*. Establish the structure of $C_{14}H_8N_2O_8$ that exists as two stable enantiomers. When reduced with iron in an

acid medium, it converts into $C_{14}H_{12}N_2O_4$. The latter compound is diazotized, with subsequent deamination, to give diphenic acid.

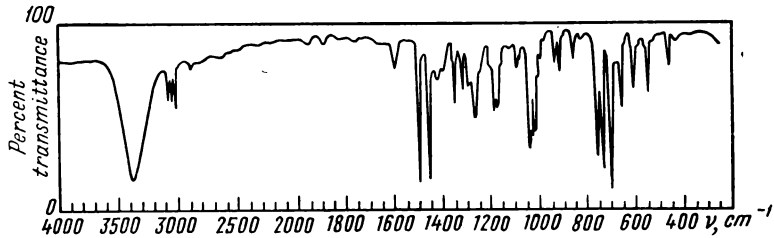
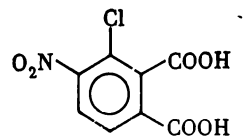


Fig. 63. I-R spectrum of $C_{13}H_{12}O$

1939. Write the structural formula of the compound $C_{10}H_6ClNO_2$, the oxidation of which gives 3-chloro-4-nitrophthalic acid



1940*. Establish the structure of the compound $C_{16}H_{13}N$ by its I-R spectrum (Fig. 64, KBr plate) and by the following:

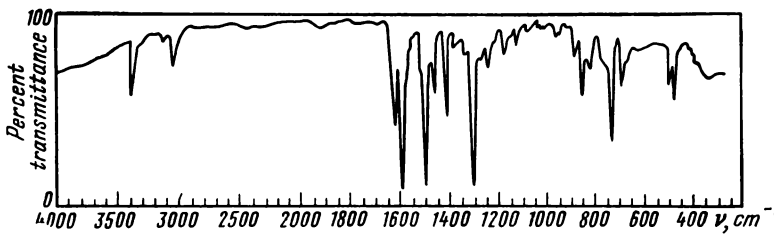


Fig. 64. I-R spectrum of $C_{16}H_{13}N$

(1) it is derived from β-naphthol and aniline, (2) reacts with nitrous acid to give $C_{16}H_{12}N_2O$. Write the reaction by which the compound $C_{16}H_{13}N$ was prepared.

1941. Establish the structure of the hydrocarbon $C_{14}H_{10}$ that is oxidized to $C_{14}H_8O_2$. The latter can be obtained by heating *o*-benzoylbenzoic acid with P_2O_5.

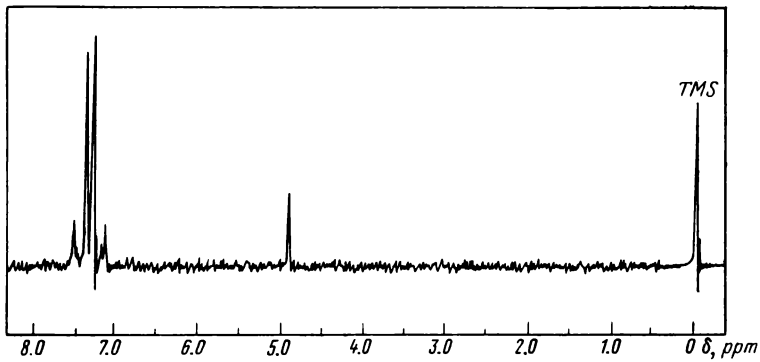


Fig. 65. NMR spectrum of $C_{14}H_9Cl_5$

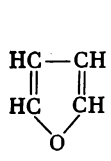
1942. Write the structural formula of a hydrocarbon having the composition $C_{14}H_{10}$ that is formed by oxidation of diphenic acid.

1943*. Establish the structure of the substance $C_{14}H_9Cl_5$ obtained by condensation of chlorobenzene with chloral hydrate in the presence of sulphuric acid. The NMR spectrum of this substance is given in Fig. 65.

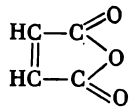
CHAPTER TWENTY-EIGHT

HETEROCYCLIC AROMATIC COMPOUNDS

1944. Name the following compounds:



a



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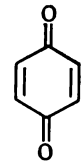

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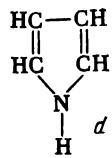

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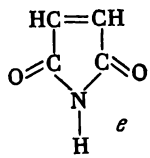
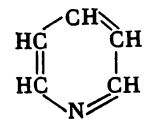


e



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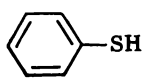

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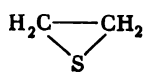
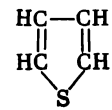


h



i

Indicate which of them are (a) heterocyclic compounds, (b) heterocyclic aromatic compounds.

1945. Write the structural formulas of: (a) benzofuran, (b) benzothiophene, (c) indole, (d) pyrazine, (e) imidazole. Why do these heterocyclic compounds have aromatic character?

1946. Atoms of which elements can take part (as hetero atoms) in the formation of aromatic heterocyclic compounds?

FIVE-MEMBERED HETEROCYCLIC COMPOUNDS

A. Methods of Manufacture

1947. Describe methods of preparing furan, thiophene, and pyrrole.

1948. Using succinic dialdehyde, synthesize furan, thiophene, and pyrrole.

1949. Accomplish the following conversions:

$$2CH_2=CH-CH_2I \xrightarrow{2Na} \ldots \xrightarrow{2O_3} \ldots \xrightarrow[-2H-C(=O)H]{2H_2O} \ldots \xrightarrow[\text{heat}]{NH_3} \ldots$$

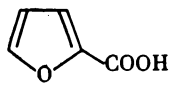
1950*. What compound is formed by the following conversions:

$$CH_2=CH-CHO \xrightarrow{(CH_3CO)_2O} \ldots \xrightarrow[[Co(CO)_4]_2,\ 125°]{CO,\ H_2} \ldots \xrightarrow[\text{heat}]{H_2O[H^+]} \ldots \xrightarrow[\text{heat}]{P_2S_5} \ldots ?$$

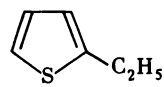
1951. Write the reaction of interconversion of furan, thiophene, and pyrrole by the Yuriev method. Specify the reaction conditions.

1952. What compound is formed by the action of dehydrating agents on 2,5-hexanedione?

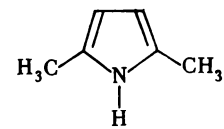
1953. Using the corresponding aliphatic compounds obtain the following derivatives of furan, thiophene, and pyrrole:



a



b



c

1954. Write the reaction used in commercial manufacture of furfural.

1955. Accomplish the following conversions:

$$\text{Acetylene} \xrightarrow[\text{catalysis, P, heat}]{2CH_2O} \ldots \xrightarrow[\text{catalysis, P, heat}]{2H_2} \ldots \xrightarrow[270°]{H_3PO_4} \ldots$$

B. Structure. Properties

1956. What structural characteristics account for the aromatic character of furan, thiophene, and pyrrole?

1957. Compare the structure and properties of the following compounds: (a) furan and tetrahydrofuran, (b) pyrrole and diethylamine, (c) thiophene and diethyl sulphide.

1958. Explain why furan is characterized by a lower conjugation energy compared with pyrrole (96.30 and 129.79 kJ/mole respectively).

1959*. Why do reactions of electrophilic substitution of furan, thiophene, and pyrrole occur predominantly in the alpha-position?

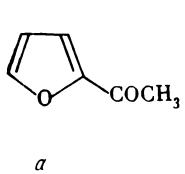
1960. Characterize the attitude of benzene and five-membered heterocycles to electrophilic reagents. Give examples of reactions and conditions for carrying them out.

1961. What sulphonating agents (oleum, 85 per cent sulphuric acid, or pyridine sulphotrioxide) are used for monosulphonation of each of the following compounds: (a) benzene, (b) thiophene, (c) pyrrole, (d) furan? Write the reactions and justify your choice.

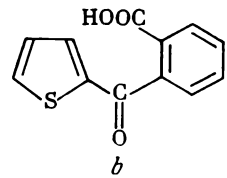
1962. Treatment of coal-tar benzene with oil of vitriol (92 per cent sulphuric acid) at room temperature purifies it from thiophene. Explain.

1963. Write the following reactions of electrophilic substitution: (a) nitration of furan with a mixture of nitric acid and acetic anhydride (at −10°C), (b) bromination of thiophene in benzene solution, (c) coupling of pyrrole with phenyldiazonium chloride. Consider their mechanisms.

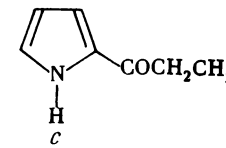
1964*. Obtain the following compounds from the corresponding non-substituted heterocycle:



a



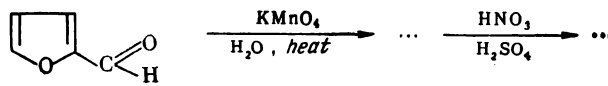
b



c

1965. What effect do electron donating and electron accepting substitutes produce on the aromatic properties of five-membered heterocycles? How do the aromatic properties of furan, α-methylfuran, and furfural compare?

1966*. Accomplish the following conversions:



Compare the structure of the end product with its I-R spectrum (Fig. 66, KBr plate).

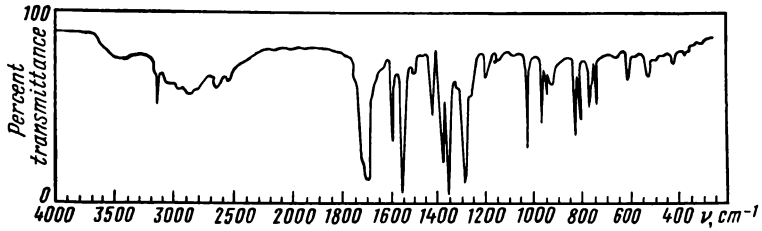
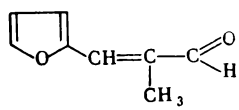


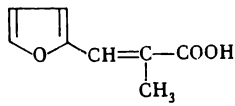
Fig. 66. I-R spectrum of the end product of furfural conversions

1967. Write the Cannizzaro reaction and furoin condensation for furfural. Consider the mechanisms of the reactions.

1968*. Use furfural to obtain the following compounds:



a



b

Consider the reaction mechanisms.

1969. Write the reactions illustrating the amphoteric properties of pyrrole. Explain the acidophobic character of pyrrole.

1970. Illustrate the chemical similarity of pyrrole and phenol.

1971. Use pyrrole to obtain the following compounds: (a) 2-pyrrole aldehyde, (b) 2-pyrrole carboxylic acid, (c) 2-methylpyrrole, (d) N-acetylpyrrole.

1972. What five-membered heterocyclic compound (furan, thiophene, pyrrole) has more manifested properties of a diene with conjugated double bonds? Write the Diels-Alder reaction of this heterocyclic compound with maleic anhydride.

1973. Write the reactions of partial and complete reduction of furan, pyrrole, and thiophene. Specify the conditions for the reactions. Name the reaction products.

1974. Compare the chemical properties of pyrrole and pyrrolidine.

1975. How can indole be synthesized? Compare the chemical properties of indole and pyrrole.

1976. Write the Fischer synthesis of 2-methylindole.

1977*. What compound is formed by the following conversions:

$$C_6H_5NH{-}NH_2 \xrightarrow{CH_3{-}\overset{\overset{O}{\|}}{C}{-}COOH} \ldots \xrightarrow{ZnCl_2} \ldots \xrightarrow{heat} \ldots$$

Compare the structure of the end product with its I-R spectrum (Fig. 67, liquid film).

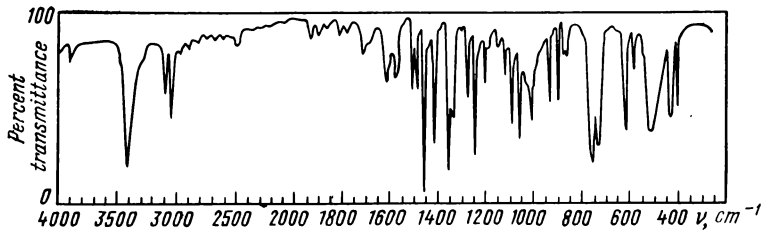


Fig. 67. I-R spectrum of the end product of phenylhydrazine conversions

1978*. What indole derivatives are formed by the Fischer reaction between the following compounds: (a) methyl ethyl ketone and 2,4-dinitrophenylhydrazine, (b) acetone and *p*-nitrophenylhydrazine, (c) cyclohexanone and phenylhydrazine?

1979*. What compound is formed by the action of ethylmagnesium bromide on indole with subsequent treatment of the reaction product with acetyl chloride?

1980*. Compare the acid properties of pyrrole, indole, and carbazole.

SIX-MEMBERED HETEROCYCLIC COMPOUNDS

1981. Indicate similarity and differences in the structure and properties of pyridine and benzene.

1982*. Characterize pyridine as a base. Write the reactions. Explain the decreased basic properties of pyridine ($pK_b = 8.96$) compared with trimethylamine ($pK_b = 4.20$).

1983. Compare basic properties of pyridine and of the product of its hydrogenation. Develop your reasons.

1984. Write the formulas of the following compounds: (a) pyridine bisulphate, (b) pyridine chloromethylate, (c) pyridine sulphotrioxide, (d) pyridine-N-oxide.

Write the reactions for preparing these compounds.

1985*. Compare the reactions of pyrrole and pyridine with strong acids in the cold. Why is pyridine not resinified when pyrrole is?

1986. Write the following reactions for pyridine: (a) sulphonation, (b) nitration, (c) chlorination. Consider the mechanisms of these reactions. Specify their conditions.

1987. Write the reaction of pyridine-N-oxide nitration. Consider the mechanism of the reaction.

1988*. Obtain 4-nitropyridine from pyridine.

1989. Bearing in mind the structure of pyridine and benzene, compare their attitude to nucleophilic reagents. Give examples of the conversions.

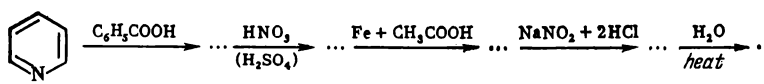
1990*. Write the reactions of pyridine with the following compounds: (a) $NaNH_2$, (b) KOH, (c) CH_3Li. Consider their mechanisms.

1991*. Use pyridine to obtain the following compounds: (a) β-bromopyridine, (b) nicotinic acid.

1992*. Compare the activity of halogen of α-, β- and γ-chloropyridines in nucleophilic substitution reactions.

1993*. Obtain all isomers of aminopyridine. Write their reactions with nitrous acid. Which of these amines forms a stable diazo compound?

1994. Complete the following:



1995. Characterize the structure and properties of α-, β-, and γ-hydroxypyridines.

1996. Why is the U-V spectrum of 4-hydroxypyridine in a neutral medium very much like the spectrum of N-methyl-4-pyridone, while in an alkaline medium it is similar to that of 4-methoxypyridine?

1997. Give examples of the following compounds: (a) a derivative of pyridine that is more reactive than pyridine in the electrophilic substitution reactions, (b) a substituted chloropyridine in which chlorine is more active than in α-chloropyridine, (c) aminopyridine that does not form stable salts of diazonium, (d) hydroxypyridine that exists in the enol form.

Establishing the Structure of Organic Compounds by Their Properties

1998. Establish the structure of $C_5H_3ClO_2$ that gives the silver mirror reaction and forms $C_5H_3ClO_3$. The latter gives α-chlorofuran on heating.

1999. Establish the structure of C_6H_6OS that has the following properties: (1) does not react with ammoniacal silver oxide, (2) gives an oxime, (3) reacts with sodium hypochlorite to give α-thiophenecarboxylic acid.

2000*. Establish the structure of $C_4H_3Cl_2N$ the hydrolysis of which gives succinimide.

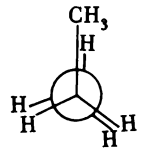
2001*. Establish the structure of $C_{11}H_{11}N$ whose oxidation with CrO_3 gives 8-quinolinecarboxylic acid.

2002*. On standing, liquid 4-chloropyridine turns into a crystalline product $C_{10}H_8Cl_2N_2$ soluble in water. What is the structure of the compound if chlorine in the '4' position is known to be very active?

2003*. Determine the structure of the compound $C_5H_4N_2O_2$ that is reduced, with subsequent reaction with nitrous acid, to give 4-pyridone.

ANSWERS AND SOLUTIONS

29. (a) 2-Methylbutyl; (b) 1,1,3-trimethylbutyl; (c) 1-methyl-1-ethyl-3-isopropylpentyl. **30.** (a) 3,3,6-Trimethyl-4-propylisobutylnonane; (b) 3,3-dimethyl-8-*tert*-butyl-5(1,1-dimethylpropyl)-dodecane. **56.** The propane molecule has two conformations:



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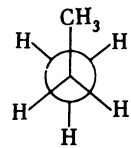
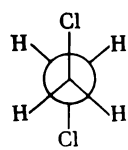
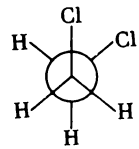


Staggered

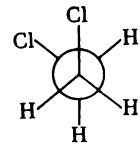
The molecule of 2,2,3,3-tetramethylbutane, like that of ethane, has two conformations. **58.** 1,2-Dichloroethane has three odd conformations: I—most stable, staggered, $\mu = 0$. Conformations II and III are skew (gauche), they are less stable and have the same energy,



I



II



III

$\mu \neq 0$. At room temperature dichloroethane exists mainly in the conformation I. The increase in the dipole moment with growing temperature is explained by the decreasing share of molecules that have staggered conformation I. The conformational equilibrium is shifted in the direction of forms II and III. **66.** The direction of the radical process can tentatively be determined from the heat effect of the reaction ΔH. Let us calculate ΔH for reactions (a) and (b). The

reaction (a): the bond C—H breaks and a new bond, H—Cl, is formed: $\Delta H = 426.36 - 430.54 = -4.18$ kJ/mole (exothermic reaction). The reaction (b): the bond C—H breaks and C—Cl bond is formed: $\Delta H = 426.36 - 334.40 = +91.94$ kJ/mole (endothermic reaction). Hence the reaction (b) is endothermic and its rate is insignificant. **67.** Halogenation of methane is the radical substitution reaction:

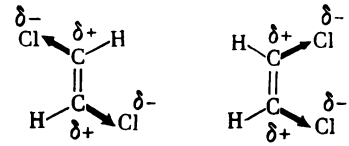
$$CH_4 + X\cdot \longrightarrow CH_3^{\cdot} + HX \quad (1) \qquad CH_3^{\cdot} + X{-}X \longrightarrow CH_3X + X\cdot \quad (2)$$

The possibility and also the character of the reaction with various halogens can be tentatively estimated by the heat effect of the reaction, ΔH. Let us first calculate ΔH for both stages of fluorination. At the first stage the bond C—H breaks and the bond H—F forms; at the second stage the bond F—F breaks and the bond C—F forms. For the stage $CH_4 + F\cdot \rightarrow CH_3^{\cdot} + HF$ $\Delta H = 426.36 - 568.30 = -141.94$ kJ/mole. For the stage $CH_3^{\cdot} + F{-}F \rightarrow CH_3F + F\cdot$ $\Delta H = 158.84 - 493.24 = -334.40$ kJ/mole. The ΔH value of chlorination, bromination and iodination can be found similarly. Let us tabulate the data:

Process	fluorination	chlorination	bromination	iodination
ΔH of the 1st stage	—137.94	—4.18	58.52	129.58
ΔH of the 2nd stage	—334.40	—91.94	—87.78	—71.06

The comparison of heat effects of the reactions shows that fluorination is a strongly exothermic reaction. It proceeds very easily (in normal conditions it is accompanied by degradation of the substance). Chlorination is also an easily going exothermic reaction, but bromination is more difficult to realize (compared with chlorination). The reaction first stage is endothermic. Iodination reaction is practically absent because of the highly endothermic first stage of the process. **68.** There is no reaction since its first stage is strongly endothermic and high energy is required: $\Delta H = 346.94 - 280.06 = +66.88$ kJ/mole (see answers to Problems 66 and 67). **72.** Isopentane has 1 tertiary, 2 secondary and 9 primary C—H bonds. One tertiary C—H bond makes 22 per cent of the chlorination product, one secondary bond makes 14 per cent and one primary, 50/9 = 5.5 per cent. The relative reactivity of the primary, secondary and tertiary C—H bonds is 5.5:14:22 respectively (i.e. 1:2.5:4). **73.** (a) Butane has 6 primary and 4 secondary C—H bonds. Let us assume the primary halide content as x%. Then $(6 \times 1)/(4 \times 32) = x/(100 - x)$, $x = 4.5$ per cent. The primary butyl bromide is 4.5 per cent and the secondary, 95.5 per cent; (b) the content of the primary and tertiary halides that are formed in bromination of isobutane can be calculated similarly. The per cent content of the primary halide is about 0.6 and of the tertiary, 99.4. **83.** 2,2,4,4-Tetramethylpentane. **106.** The conformational interconversions of alkanes occur without cleavage of the σ-bond; *cis-trans*-isomerization is accompanied by the cleavage of the pi-bond and high energy is therefore required. **111.** The differences are explained by that the vector total of the dipoles formed by the polarized bonds

C→Cl for the *trans*-isomer is, and for the *cis*-isomer is not equal to zero:



trans- $\mu = 0$ *cis*- $\mu = 1.89\,D$

112. *trans*-Isomers have high symmetry and are more stable than *cis*-isomers (less energy in store). Hence the heat of hydrogenation of *trans*-2-pentene should be less (115.37 kJ/mole) than of *cis*-isomer (119.55 kJ/mole) since the formed pentane has even lower free energy. **121.** One of the factors that proves the stepped electrophilic character of bromine addition to alkenes is the formation of mixed addition products. If the bromination reaction is effected in the presence of NaCl, then, in addition to the dibromide $\rangle$CBr—CBr$\langle$ is also formed the product $\rangle$CBr—CCl$\langle$. **122.** (1) See answer to Problem 121; (2) the formation of bromonium ion, as an intermediate product, is proved by stereospecificity of this reaction. **123.** See answer to Problem 121. **125.** During electrophilic addition, the rate-limiting step of the process is addition of the electrophile (Br^+). The addition is the faster, the greater the amount of electron-donating substituents at the double bond. Despite the steric hindrances, tetramethylethylene therefore adds bromine more readily than ethylene. **129.** During hydrogen halide addition to alkenes, the slow rate-determining step of the process is protonation. The addition rate therefore increases with the acidity of the reagent, i.e. in the series HCl<HBr<HI. **131.** See answer to Problem 125. In the presence of aluminium chloride, a more active electrophile (H^+) is formed by the reaction

$$HCl + AlCl_3 \rightleftharpoons \overset{+}{H}[AlCl_4]^-$$

132. See answer to Problem 125. **133.** $CH_3CHClCH_2I$. **138.** The Kharasch effect is due to the ability of HBr to add across the double bond by the radical mechanism:

$$R\cdot(\text{from a peroxide}) + HBr \longrightarrow R{-}H + Br\cdot$$

$$R'{-}CH{=}CH_2 + Br\cdot \longrightarrow R'{-}\dot{C}H{-}CH_2Br(I)$$

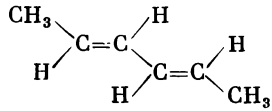
$$R'{-}\dot{C}H{-}CH_2Br(I) + H{-}Br \longrightarrow R'{-}CH_2{-}CH_2Br(II) + Br\cdot \text{ etc.}$$

As HBr is added, the reaction of formation of products (I) and (II) is exothermic. With HI, the atom $:\dot{\underset{\cdot\cdot}{\overset{\cdot\cdot}{I}}}:$ is readily formed, but its reacti-

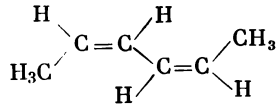
vity is insufficient to initiate the chain reaction. The reaction of HCl addition is closer to reactions with HBr with respect to the energy characteristics. **141.** Reaction of electrophilic addition of hypochlorous acid HClO with the formation of ethylene chlorohydrin $ClCH_2$—CH_2OH. **163.** The product of allylic bromination in the 4-position is mainly formed:

$$(CH_3)_2C{=}CH{-}CHBr{-}CH_3$$

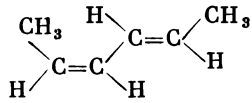
170. Olefin $C_{10}H_{20}$. **171.** C_8H_{16}. **173.** $(CH_3)_2CH{-}CH{=}CH{-}CH(CH_3)_2$. **174.** 3-Methyl-1-butene. **180.** (a) None; (b) two, (c) three:



trans, trans-

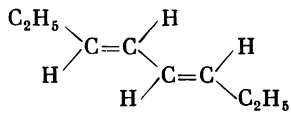


cis, cis-

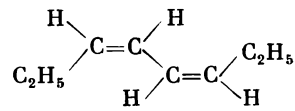


cis, trans-

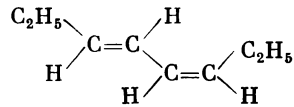
181.



trans, trans-



cis, cis-



cis, trans-

186. (a) By catalytic dehydrogenation of isopentane; (b) according to the following reactions:

$$(CH_3)_2CH{-}CH_2CH_3 \xrightarrow[-HCl]{+Cl_2} (CH_3)_2CClCH_2CH_3 \xrightarrow{-HCl}$$

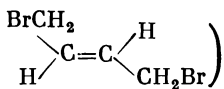
$$\rightarrow (CH_3)_2C{=}CH{-}CH_3 \xrightarrow{+Cl_2} (CH_3)_2CCl{-}CHClCH_3 \xrightarrow{-2HCl}$$

$$\rightarrow CH_2{=}C(CH_3){-}CH{=}CH_2$$

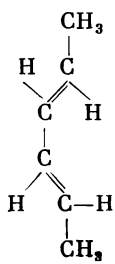
194. The molecular refractivity of these hydrocarbons, calculated as the sum of refractivities of all bonds (10 C—H, 3 C—C, 2 C=C) is 28.99. For hydrocarbon (a) having isolated double bonds, MR_D,

both calculated and obtained experimentally, are the same. For hydrocarbon (b) with conjugated double bonds MR_D found experimentally is 1.65 greater compared with that calculated (exaltation of molecular refractivity). **198.** 1,4-Pentadiene contains two isolated double bonds. The heat of its hydrogenation is therefore twice as much as that of 1-butene. 1,3-Butadiene is a more stable system because of conjugation of the π-bonds. The conjugation energy is about 15 kJ/mole. The heat of hydrogenation of 1,3-butadiene is a doubled heat of hydrogenation of 1-butene minus the above 15 kJ/mole. **200.** Conjugated dienes are reduced with sodium metal in alcohol to dihydrogen derivatives whereas isolated dienes and simple olefins are not reduced in these conditions. This is explained by that in the addition reactions the transition state of conjugated dienes has the allylic structure which is characterized by lower formation energy due to conjugation. **201.** Only the system of conjugated double bonds is reduced in these conditions. Predominantly formed is the diene having the structure $CH_3CH{=}C(CH_3)CH_2CH_2CH{=}C(CH_3)_2$, which is oxidized in strict conditions to give acetic acid, acetone, and keto acid, $CH_3CO{-}CH_2CH_2COOH$. **203.** The addition of electrophile (Br^+) at the rate-determining step of the process is the easier, the greater the amount of electron-donating groups at the carbon atoms that form double bonds. The following compounds are predominantly formed: (a) $CH_3CHBrCHBrCH_2CH{=}CHBr$ and (b) $(CH_3)_2CBrCHBrCH_2CH{=}CH_2$.

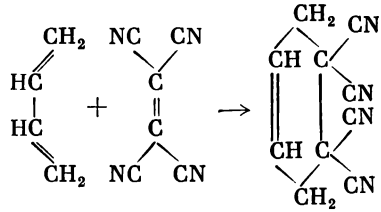
205. It has been established that *trans*-isomer (in our case



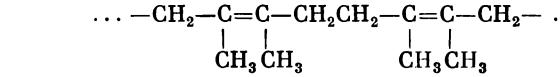
) is formed in reactions of 1,4-addition. If bromine were added in one step, *cis*-isomer would be the reaction product. **206.** The relative amounts of 1,2- and 1,4-addition products depend on the temperature, nature of the solvent, and the length of the process. The 1,4-addition product is more stable and predominates in an equilibrium mixture in normal conditions. The 1,2-addition product is formed faster and predominates if the reaction temperature is low. **207.** See answer to Problem 206. **213.** The Diels-Alder reaction is characterized by high stereospecificity. Diene reacts in the form in which its double bonds are in the S-*cis* conformation. In substituted dienes, *cis*-alkyl groups produce appreciable blocking action. Out of 2,4-hexadiene isomers, it is the *trans*,*trans*-2,4-hexadiene in the S-*cis* conformation that easily enters the Diels-Alder reaction:



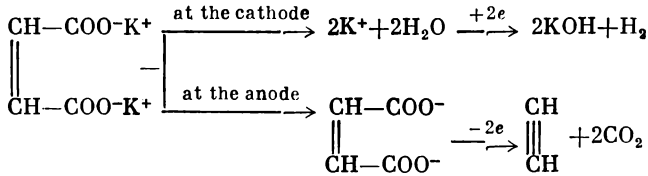
214. The Diels-Alder reaction occurs. Tetracyanoethylene (dienophile) is added to 1,3-butadiene in the 1,4-positions:



221. 2,3-Dimethyl-1,3-butadiene was taken as the monomer. A fragment of the polymer chain (the addition of the monomer molecules in the 1,4-positions) is given below:



232. 1,3-Butadiene. **237.** (a) 1-Undecaene-3,5,7,9-tetrayne; (b) 1,11-tridecadiene-3,5,7,9-tetrayne. **246.**



253. The different acid properties of ethane, ethylene and acetylene molecules depend on the character of hybridization of the atomic orbitals of their C—H bonds (sp^3, sp^2, sp, respectively). The *s*-character is stronger in those sp^n-hybrid orbitals in which the orbital shape is closer to spheric; in the *sp*-hybrid form, the electrons are closer to the nucleus and are retained relatively stronger, while the hydrogen atom of the C—H bond becomes more positive and is easier to abstract by the action of the proton acceptors. **254.** The acid properties of acetylene and hydrogen cyanide depend on the *sp*-hybrid state of the carbon atoms. The stronger acid properties of HCN are explained by the electron-accepting character of the CN group which promotes additional polarization of the C—H bond. **260.** The compounds (a) and (c) can be differentiated by their I-R spectra, and the compounds (b) can be distinguished by their U-V spectra. **261.** The I-R spectrum corresponds to the compound (c). **263.** (a) Catalytic hydrogenation is a stereospecific reaction and gives *cis*-olefin; (b) the electrophilic addition reaction (via bromonium cation) is stereospecific as well and gives *trans*-isomer. **264.** See answer to Problem 263. **266.** The triple C—C bond is less susceptible to the attack by electrophilic reagents than the double bond. This, in part, is due to the fact that *sp*-hybrid atoms

of triply bonded carbon atoms are much more electronegative than sp^2-hybrid atoms of the double-bonded carbon atoms, and π-electrons of the C≡C bond are retained by the carbon atom nuclei faster than the π-electrons of the C=C bond. **269.** (c) Via ethylacetylene with subsequent addition of HCl and HBr. **271.** (c)

$$C_2H_5C{\equiv}CH \xrightarrow{HOBr} \left[C_2H_5C(OH){=}CHBr\right] \xrightarrow{HOBr} \left[C_2H_5C(HO)(OH){-}CHBr_2\right] \xrightarrow{-H_2O}$$

$$\longrightarrow C_2H_5{-}\overset{\overset{O}{\|}}{C}{-}CHBr_2$$

276. Accomplish, step by step: dehydrobromination, bromination, dehydrobromination again, and hydration by the Kucherov method. **277.** (b) The product of addition of 1 mole of bromine has *trans*-configuration. **289.** The Kucherov hydration and subsequent ozonolysis of the obtained unsaturated ketone. **290.** Isopropylacetylene. **302.** The haloform reaction is characteristic of the carbonyl compounds having the structure R—CO—CH_3, and also of alcohols of the R—CHOH—CH_3 type, where R is H or alkyl. **309.** The most suitable method of differentiating between (a) and (b) is NMR spectroscopy. **315.** Basicity is the affinity for proton, and nucleophilicity is the ability to form bonds with electrophilic carbon atom. Basicity is normally measured by the dissociation constant of a given base in water, while nucleophilicity, by the reactivity in S_N2 reactions with methyl bromide in water. Nucleophilicity of anions depends on the electron density on the attacking atom (basicity) and on the polarizability of electrons. It is necessary also to bear in mind the nature of the solvent in which the reaction occurs (solvation). If the attacking atom is the same, nucleophilicity of an anion is correlated with its basicity, e.g.

$$CH_3{-}\overset{\overset{O}{\|}}{C}{-}O^- < HO^- < CH_3O^-$$

If groups containing different nucleophilic centres are to be compared, nucleophilicity is in direct proportion with their polarizability, e.g. $F^- < Cl^- < Br^- < I^-$ (in water). **317.** Inversion of configuration occurs here. **319.** Tertiary alkyl halides enter with difficulty the S_N2 reactions because of steric hindrances produced by alkyl groups during the attack on the nucleophile from the side opposite to that of the leaving group. **322.** (a) The strongest base is RO^-; (b) the strongest nucleophile is I^-. See also explanations to Problem 315. **323.** Acetate ion is a stronger nucleophile than water but weaker than hydroxyl ion. See answer to Problem 315. **324.** The reaction rate increases with growing nucleophilicity of the reagent: $CH_3COO^- < OH^- < I^-$. **325.** Both reactions are the S_N2 type. The higher rate of the reaction (b) is explained by the higher nucleophilicity of the anion n-$C_4H_9S^-$, compared with n-$C_4H_9O^-$. **326.** Hydrolysis of primary alkyl chlorides in the presence of I^- proceeds as two consecutive S_N2 reactions:

(1) under the influence of the strong nucleophile I^- the primary alkyl chloride converts into the corresponding iodide:

$$R{-}CH_2Cl + I^- \longrightarrow R{-}CH_2{-}I + Cl^-$$

(2) the formed alkyl iodide easier enters the hydrolysis than the starting compound (the leaving group effect):

$$R{-}CH_2{-}I + H_2O \longrightarrow R{-}CH_2OH + HI$$

327. CH_3Br reacts practically only according to the S_N2 mechanism, while for neopentyl bromide, the S_N2 reactions are difficult to realize because of steric hindrances. In conditions favourable for the S_N1 reactions, neopentyl bromide reacts with modifications in the carbon skeleton. For example, during hydrolysis it forms *tert*-amyl alcohol which is due to the rearrangement of the primary carbonium ion I, which is first formed, into more stable tertiary ion II:

$$\underset{\text{I}}{CH_3{-}\overset{\displaystyle CH_3}{\overset{|}{C}}{-}CH_2^+} \longrightarrow \underset{\text{II}}{CH_3{-}\overset{\displaystyle CH_3}{\overset{|}{\underset{+}{C}}}{-}CH_2CH_3}$$

331. The intermediate compound, tertiary carbonium cation $CH_3CH_2{-}\overset{+}{(CH_3)C}{-}CH_2CH_2CH_3$, has a planar structure. An attack on it by a nucleophilic reagent is possible on both sides of the plane, and the resultant product will therefore be optically inactive (racemization). **334.** The hydrolysis occurs easier in an aqueous-alcoholic medium since in S_N1 reactions that solvent is most active which solvates both cations and anions, i.e. water, alcohol, and the like. Ether solvates only cations. **335.** This is the S_N1 reaction, the rate of which does not depend on the concentration or nature of the nucleophile. Conditions (b) are the most suitable. Acetic acid acts as a solvent and a reagent. It is reasonable to add water since it is more polar than acetic acid and will therefore promote formation and stabilization of carbonium ion. **339.** Nucleophilic properties of the neutral molecule C_2H_5OH are less marked than of the corresponding anion $C_2H_5O^-$. As isopropyl bromide and alcohol are heated, a slow nucleophilic substitution (S_N2) occurs that gives the ether $(CH_3)_2CH{-}O{-}C_2H_5$. If isopropyl bromide is heated with sodium ethoxide, propylene is the main reaction product ($E2$ reaction). **340.** The stronger the basic properties of a nucleophile, the stronger its dehydrohalogenating power:

$$H_2O < C_2H_5OH < CH_3CH_2O^- < (CH_3)_2CHO^- < (CH_3)_3CO^-$$

343. *trans*-2-Pentene. **345.** As a rule, $E2$ reactions predominantly give the most stable alkene, i.e. the most branched alkene (the Zaitsev rule). The rule holds for 2-bromo-2-methylbutane. In the second case the elimination gives mostly a less branched alkene due to a strong shielding of the CH_2 grouping with methyl radicals (the Hofmann rule). **346.** (a) Heating with water in the presence of damp silver oxide

(S_N1 mechanism). Side reactions (elimination of HBr and formation of ether) that occur as a result of the action of water on alkyl halide in the presence of an alkali and an alcohol can be avoided. The alcohol would be usually added to dissolve the alkyl halide. (b) Heating with KI in acetone (Finkelstein reaction, S_N2 mechanism). (c) Heating with an alcoholic solution of alkali. Using a strong base of moderate nucleophilicity (OH^-) and an alcohol as a solvent (its polarity being less than that of water) promotes elimination ($E2$ mechanism). (d) Heating with potassium *tert*-butylate in alcohol. Branching and strong basic properties of the *tert*-butylate anion are responsible for the $E2$ mechanism of the reaction with the formation of a less branched alkene. **357.** The dipole moment of ethyl bromide is determined by the polarity of the bond $\overset{\delta+}{C} \rightarrow \overset{\delta-}{Br}$ due to the $-I$ effect of bromine atom. The polarity of this bond in vinyl bromide is decreased by the conjugation effect acting in the opposite direction (interaction of the unshared pair of electrons of the halogen atom with pi-electrons of the double bond). Hence: $\mu CH_2{=}CH{-}Br < \mu C_2H_5{-}Br$. Vinyl bromide, therefore, unlike ethyl bromide, has very low activity in nucleophilic substitution reactions. **358.** Because of the strong $-I$ effect of chlorine atom, vinyl chloride must add HBr contrary to the Markownikoff rule (static factor). But in reality the addition obeys the Markownikoff rule:

$$CH_2{=}CH \longrightarrow \ddot{\underset{\cdot\cdot}{Cl}}: + HBr \longrightarrow CH_3{-}CHClBr$$

This can be explained by the fact that at the moment of the reaction it is the stability of the intermediate carbonium ion (dynamic factor) that determines the character of the reaction. Out of the two possible cations:

$$CH_3 \longrightarrow \overset{+}{C}H \longrightarrow \ddot{\underset{\cdot\cdot}{Cl}}: \text{ (I) } \textit{and } \overset{+}{C}H_2{-}CH_2 \longrightarrow \ddot{\underset{\cdot\cdot}{Cl}}: \text{ (II)}$$

the more stable carbonium cation I is formed (its charge is partly compensated by the shift of the unshared electrons of the chlorine atom and also by the electron-donating methyl group). Effect of the static factor is manifested in the lowered (compared with the unsubstituted ethylene) rate of addition of HBr across the double bond. **363.** Allyl halides easier enter the S_N1 and S_N2 reactions compared with the corresponding saturated halogen derivatives. The easiness with which allyl halides enter S_N1 reactions is explained by the formation of a stable (due to conjugation) carbonium cation:

$$CH_2{=}CH{-}CH_2\,Cl \rightleftharpoons \left[CH_2{=}CH{-}\overset{+}{C}H_2 \longleftrightarrow \overset{+}{C}H_2{-}CH{=}CH_2 \right] + Cl$$

365. See answer to Problem 363. 367. (b) The direction of electrophilic addition of HBr is determined by the presence of the $-C\begin{matrix}\nearrow Cl\\ \rightarrow Cl\\ \searrow Cl\end{matrix}$ group having a strong $-I$ effect and the reaction does not obey the Markownikoff rule. 368. (a) $CH_2=CH-CH_2Cl + HBr \rightarrow CH_3-CHBr-CH_2Cl$ (according to the Markownikoff rule); (b) $CH_2=CH-CH_2Cl + HBr \xrightarrow{\text{peroxide}} CH_2Br-CH_2-CH_2Cl$ (contrary to the Markownikoff rule).

369.

$$CH_2=CH-CH_2Br \xrightarrow{Br_2} CH_2Br-CHBr-CH_2Br \xrightarrow[\text{alcohol, } -HBr]{NaOH\ (1\ mole)} \rightarrow CH_2Br-CBr=CH_2 \xrightarrow[-MgBr_2]{C_2H_5MgBr} CH_2=CBr-CH_2CH_2CH_3$$

371. Crotyl bromide is isomerized into 3-bromo-1-butene:

$$CH_3-CH=CH-CH_2Br \underset{\longleftarrow}{\xrightarrow{100^\circ}} CH_3CHBr-CH=CH_2$$

The isomerization is due to the formation of an intermediate mesomeric carbonium ion capable of reacting with nucleophile (Br^-) at two electrophilic centres (1 and 3):

$$\overset{3}{CH_3}-\overset{2}{CH}=\overset{1}{CH}-\overset{+}{CH_2} \leftrightarrow CH_3-\overset{+}{\underset{3}{CH}}-\overset{2}{CH}=\overset{1}{CH_2}$$

372. Nucleophilic substitution of allyl halide is accompanied with partial allylic rearrangement:

$$CH_2=CH-CHCl-CH_3 \xrightarrow[-HCl]{H_2O} \begin{matrix}\nearrow CH_2=CH-CH(OH)-CH_3 & \text{normal product}\\ \searrow HOCH_2-CH=CH-CH_3 & \text{product of the rearrangement}\end{matrix}$$

The reaction proceeds via the formation of a carbonium ion of the allyl type. See answer to Problem 371. 373. (1) $CH_2=C(CH_3)-CH(CH_3)-OCH_3$; (2) $CH_2(OCH_3)-C(CH_3)=CH-CH_3$. See also answer to Problem 372.

375.

(a) $C_7H_{16} + 16CoF_3 \rightarrow C_7F_{16} + 16CoF_2$

$CHCl_3 + 2HF \rightarrow CHClF_2 + 2HCl$

(b) $2CHClF_2 \xrightarrow{600-800^\circ} CF_2=CF_2 + 2HCl$

(c) $CH_3-CH=CH_2 + HF \xrightarrow{0^\circ} CH_3-CHF-CH_3$

378. Fluorine atoms bonded to the same carbon atom inactivate each other (due to the strongly negative inductive effect of the fluorine atom). **386.** $CH_3CH_2CCl_2CH_2CH_2CH_3$. **388.** $CH_2{=}CH{-}CHBr{-}CH_3$; the hydrolysis of this bromide is accompanied by the allylic rearrangement that gives the alcohols $CH_2{=}CH{-}CH(OH){-}CH_3$ and $CH_2(OH){-}CH{=}CH{-}CH_3$. **389.** $CH_2Cl{-}CHCl_2$. **390.** 1,1,2,3,3-Pentachloropropane. **391.** $ClCH_2{-}C{\equiv}C{-}CH_2Cl$. **397.** Reactions (b) and (d) are possible, since in both cases the organometallic compound reacts with a more electropositive metal. **403.**

$$BrCH_2COOC_2H_5 \xrightarrow{Zn} Br{-}Zn{-}CH_2COOC_2H_5 \xrightarrow{CH_3CH_2C(=O)H} \longrightarrow CH_3CH_2CH(OZnBr){-}CH_2COOC_2H_5 \xrightarrow[-ZnBr(OH)]{H_2O} CH_3CH_2CH(OH){-}CH_2COOC_2H_5$$

406. Organomagnesium compound is solvated with ethyl ether molecules. **413.**

(a) $CH_3CH_2CH_2CH_3 + CH_3O{-}SO_2OMgI$

(b) $CH_3{-}C{\equiv}C{-}CH_2CH_2CH_3 + MgBr_2$

(c) $CH_3CH_2CH_2CH_2{-}O{-}CH_3 + MgBrCl$

414. $CH_3CH_2CH_2MgBr + I{-}I \rightarrow CH_3CH_2CH_2I + MgBrI$. **421.** Vinylmagnesium bromide is prepared by the reaction between vinyl bromide and magnesium in tetrahydrofuran (Normant reaction):

$$CH_2{=}CH{-}Br + Mg \xrightarrow{\text{tetrahydrofuran}} CH_2{=}CH{-}MgBr$$

424.

$$H{-}C(=O){-}OC_2H_5 + CH_3MgBr \longrightarrow H{-}C(OMgBr)(OC_2H_5){-}CH_3 \xrightarrow[-C_2H_5OMgBr]{CH_3MgBr} \longrightarrow H{-}C(OMgBr)(CH_3)_2 \xrightarrow[-MgBr(OH)]{H_2O} CH_3CH(OH)CH_3$$

425. Because of lower reactivity, the reaction of organocadmium compounds stops at the stage of formation of a ketone while with the Grignard reagent the process proceeds further with the formation of a tertiary alcohol. **429.** This is explained by the higher polarity of the

group $\diagdown C{=}O$ (as compared with the polarity of the double carbon-carbon bond). **430.** The compound (a) is formed by the hydrolysis of the addition product of C_2H_5MgBr to 3-pentene-2-one in the 1,4-positions $\left(CH_3\overset{2}{C}(=O^1)-\overset{3}{H}C=\overset{4}{C}H-CH_3\right)$, and the compound (b) is formed by the hydrolysis of the addition product in the 1,2-positions. **431.** Granosan is obtained by the following equation:

$$2C_2H_5Cl \xrightarrow{2Na-Hg} (C_2H_5)_2Hg+Hg+2NaCl$$

$$(C_2H_5)_2Hg+HgCl_2 \longrightarrow 2C_2H_5-Hg-Cl$$

444. 3,7-Dimethyl-2,6-octadiene-1-ol. Two geometric isomers. **463.** Alcohols (a) and (b). **470.**

(a) $CH_3(CH_2)_{10}CH_2OH+C_2H_5OH$

(b) $CH_3(CH_2)_7CH{=}CH(CH_2)_7CH_2OH+C_4H_9OH$

(c) $(HO)CH_2-(CH_2)_4-CH_2(OH)+2C_2H_5OH$

474. By the reaction of allylmagnesium chloride with: (a) acetaldehyde; (b) acetone with subsequent hydrolysis of the reaction products. **494.** The differences are due to relatively low polarizability of the C—O bond in alcohols compared with polarizability of the C—halogen bond. (R_D of the bonds are: C—O 1.54, C—Cl 6.51, C—Br 9.39, C—I 14.61.) The catalytic role of the acid consists in the transfer of a proton to the atom of the alcoholic oxygen:

$$R-\ddot{O}-H+H^+ \rightleftharpoons R-\overset{+}{O}H_2$$

The protonation of the alcohol converts the OH group into a relatively easily leaving group (H_2O). **497.** Nucleophilic properties of Br^- are stronger than of Cl^-.

499.

$$3CH_3(CH_2)_5CH(OH)-CH_3+PI_3 \longrightarrow 3CH_3(CH_2)_5CHI-CH_3+H_3PO_3$$

As iodine derivatives are prepared from the alcohol and HI, the latter can reduce the formed alkyl iodide to a hydrocarbon. **501.** Rates of esterification of various alcohols (with the same acid) strongly depend on steric hindrances and decrease in the following series: methyl alcohol > isopropyl alcohol > *tert*-butyl alcohol. **507.** Dehydrochlorination of butyl chloride with alcoholic solution of alkali is an irreversible reaction. Dehydration of butyl alcohol with sulphuric acid is a reversible process and gives therefore a mixture of isomers:

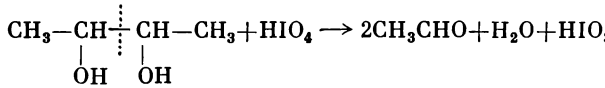
$$CH_3CH_2CH_2CH_2OH \xrightarrow[\text{heat, } H_2O]{H_2SO_4} CH_3CH_2CH{=}CH_2 \overset{+H^+}{\rightleftharpoons} CH_3\overset{+}{C}H_2CHCH_3$$

$$\downarrow\uparrow -H^+$$

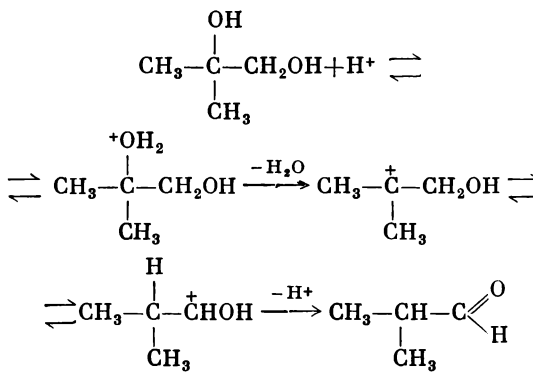
$$CH_3CH{=}CHCH_3$$

517. The conversion of vinyl alcohol into acetaldehyde is connected with the gain in energy of 62.7 kJ/mole. **521.** Alcohol (a) is more reactive since it gives an intermediate which is a more stable (stabilized by conjugation) carbonium cation:

522. In addition to the normal product of nucleophilic substitution of bromine atom (85 per cent) for the OH group, alcohol (b) forms also a small quantity of the product of allylic rearrangement. **528.** Periodic acid is a specific reagent for 1,2-glycols. It breaks the C—C bond to give two molecules of aldehydes (or ketones) according to the following reaction:



530. Pinacolin, $CH_3-\overset{\overset{O}{\|}}{C}-C(CH_3)_3$ is formed. **533.** The mechanism of the last stage is similar to that of the pinacol rearrangement of alpha-glycols:



535. By dehydration with subsequent ozonolysis of the products of dehydration. **540.** Figure 7 shows the spectrum of isobutyl alcohol. **542.** $CH_3CH_2\underset{\underset{CH_3}{|}}{C}(OH)-\underset{\underset{CH_3}{|}}{C}(OH)CH_2CH_3$. See answer to Problem 528.

544.

1. $CH_2(OH)-CH(CH_3)-CH=CH_2$
2. $CH_3-\underset{\underset{CH_3}{|}}{C}(OH)-CH=CH_2$
3. $CH_2=C(CH_3)-CH(OH)CH_3$
4. $CH_2=C(CH_3)-CH_2CH_2OH$

545. Allyl alcohol. **546.** Isopropyl alcohol. **551.** Alcohol dehydration with the formation of olefins occurs as a side process. Primary alcohols give high yields of ethers, secondary alcohols give much olefins and di-*tert*-alkyl ethers fail to be obtained by this method (only olefins are formed). **553.** Methyl isopropyl ether should be obtained by the action of methyl bromide on sodium isopropylate:

$$CH_3—Br+(CH_3)_2CH—O^-Na^+ \longrightarrow CH_3—O—CH(CH_3)_2+NaBr$$

Another way is the reaction of isopropyl bromide with sodium methoxide, but the method is insufficient since a side process, the formation of propylene, will take place.

554. (a) $CH_3CH_2OC_4H_9$ + NaBr (S_N2 reaction).

(b) $(CH_3)_2C=CH_2+C_2H_5OH+NaBr$ ($E2$ reaction).

See answer to Problem 553. **555.** The action of silver oxide on *tert*-butyl iodide. The former two methods give isobutylene. **557.** The end product is divinyl ether, $CH_2=CH—O—CH=CH_2$.

566. (b) $(C_2H_5)_2\overset{+}{O}—\overset{-}{B}F_3$; (c) $\left[\begin{matrix}CH_3—O—CH_3\\ \quad\quad|\\ \quad\quad H\end{matrix}\right]^+BF_4^-$.

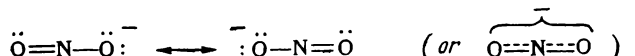
568. For mixed ethers, the direction of cleavage depends on the reaction mechanism and the structure of alkyls. Ether (a) is split by the S_N2 mechanism (primary alkyls):

$$CH_3—O—CH_2CH_3+HI \xrightarrow{S_N2} CH_3I+C_2H_5OH$$

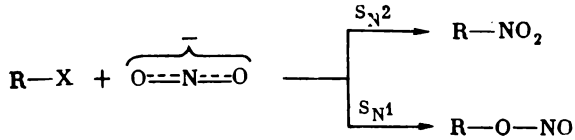
The ethyl group, being more hindered to the attack by the nucleophile (I^-) remains linked with oxygen. *tert*-Butyl group can form relatively stable carbonium ion; ether (b) reacts therefore by the S_N1 mechanism (the O-*tert*-butyl bond breaks down):

$$CH_3—O—C(CH_3)_3+HI \xrightarrow{S_N1} CH_3OH+(CH_3)_3C—I$$

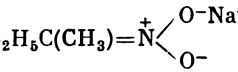
570. In hexane HBr is added to an olefin faster than in ethyl ether. This is explained by the fact that HBr reacts with ethyl ether to give an oxonium compound. **576.** By shaking the mixture with sulphuric acid in the cold. The ether turns into an oxonium compound soluble in sulphuric acid. **578.** I-R spectroscopy for compounds (a) and (b) and NMR spectroscopy for compound (c). **589.** The lower boiling point of methyl mercaptan (compared with methyl alcohol) is explained by the weak association of mercaptan molecules. Dimethyl sulphide boils at higher temperatures than mercaptan since its molecular weight is higher. **600.** Methyl ethyl sulphide, $CH_3—S—C_2H_5$. **607.** The anion of nitrous acid has the following structure:



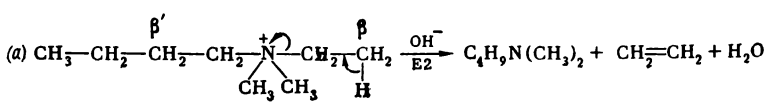
The oxygen atom is the locus of the highest electron density, and the nitrogen atom has the highest nucleophilicity. In conditions of the S_N2 reactions, the nucleophile NO_2^- attacks the substrate by the nitrogen atom to give a nitro compound. In the S_N1 reactions, the formed carbonium ion reacts with a more electronegative oxygen atom of the anion NO_2^- to give an ester of nitrous acid:



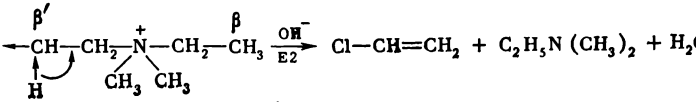
Said reaction conditions for 1-bromobutane with $AgNO_2$ in ether are favourable for the S_N2 mechanism (primary halide, nonpolar solvent); the main product of this conversion will therefore be 1-nitrobutane. A small amount of butyl nitrite is also formed as a side product. **608.** 1-Iodopropane reacts with $AgNO_2$ in ether (mainly the S_N2 mechanism). In the case with 2-iodopropane, the electrophilic action of silver ion shifts the reaction into the S_N1 region. See also answer to Problem 607. **609.** The reaction is the S_N2 type, with predominant formation of 1-nitropropane. Dimethyl formamide is a strongly polar aprotic solvent. It weakly solvates anions and does not therefore promote the S_N1 reactions, but accelerates the S_N2 reactions. Tertiary halides give olefins in these conditions. **610.** The highest yield of the nitro compound will be in the latter case since the conditions for the S_N2 reactions are most favourable in this case. **611.** See answer to Problem 609. **627.** The end product is 2-nitrobutane. **631.** (a) $HOCH_2—C(CH_3)_2—NO_2$; (b) $(HOCH_2)_3C—NO_2$. **633.** (b) The end product is $CH_3CH_2CH(Br)—NO_2$. **635.** Use the Konovalov-Nef reaction. **638.**



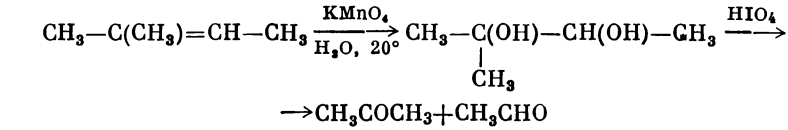
639. $(CH_3)_2CH—CH_2NO_2$. **640.** 1-Nitropropane. **641.** $(HOCH_2)_3CNO_2$. **652.** Use the Gabriel reaction between a halogen derivative and potassium phthalimide. **658.** The method (a) gives an olefin. **663.** The absence of optical activity is explained by continuous oscillation of the amine molecule. **666.** The activity of hydrogen at the alpha-carbon atom of nitro compounds is explained by the strong $-I$ effect of the nitro group. **669.** I-R spectroscopy. **676.** Quaternary ammonium bases are split by the $E2$ mechanism to give a tertiary amine and an olefin; the group capable to form an olefin with the least possible number of alkyl groups at the double bond, undergoes predominantly beta-elimination (Hofmann's rule):



The electron-donating substituent (CH_3CH_2) at the β′ carbon atom prevents β′-elimination. The acceptor substituent (chlorine atom) at the β′-carbon atom, on the contrary, promotes selective β′-elimination.



681. Triethylamine oxide, having a tetrahedral structure and semipolar nitrogen-oxygen bond, is formed. 688. Diethylamine. 689. $(CH_3)_2CH-CH_2-CH_2-NH-CH_3$. 690. $CH_3CH_2CH(CH_3)-CH_2-NO_2$. 691. Dimethyl-*tert*-butylamine. 699. 3,7-Dimethyl-2,6-octadienal exists in the form of *cis*- and *trans*-isomers. 710. (a) $2CH_3CHO$; (b) $HC(=O)H + CH_3COC_2H_5$. See also answer to Problem 528. 711.

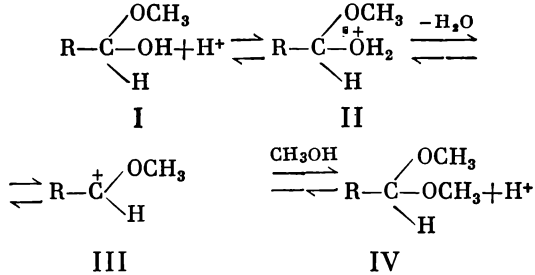


712. Carry out the following reactions: dehydration, oxidation of the obtained olefin in the conditions of the Wagner reaction, and splitting of 1,2-glycol with periodic acid. 734. Catalytic hydrogenation of both butyraldehyde and crotonaldehyde gives 1-butanol. Lithium aluminium hydride is a selective reducing agent: it readily reduces the carbonyl group to the alcoholic group but fails to reduce the double carbon-carbon bond. 736. This is the nucleophilic addition reaction. The formation of cyanohydrins is accelerated by adding bases since the latter promote the formation of a strong nucleophilic reagent (CN^-). 739. The difference is explained by that HCN is a weaker nucleophile than $NaHSO_3$. 746. The stability of chloral ammonia is explained by the strong electron-accepting character of the trichloromethyl group. 748. The aldol condensation can serve as an example. The activity of hydrogen at the alpha-carbon atom depends on the ability of the aldehyde to form a stable (stabilized by conjugation) anion. 752. If two different carbonyl compounds enter the aldol condensation, one of them reacts with the base to give enolate anion, whereas the other adds this anion across the carbonyl group. In our problem one of the starting compounds is formaldehyde which can react only with the enolate ion across the carbonyl group because of the absence of alpha-hydrogen atoms. The reaction products are as follows:

(a) $CH_2(OH)CH_2COCH_3$, (b) $CH_2(OH)C(CH_3)_2-CHO$

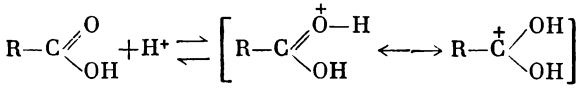
753. Oxidation of the starting alcohol to the aldehyde and subsequent croton condensation of this aldehyde. 754. The starting substances: (a) acetaldehyde and acetone, (b) acetaldehyde and butanol, (c) *n*-butyraldehyde and acetone. In condensation of an aldehyde with a ketone,

the former usually reacts as a carbonyl component, while the latter (due to lower activity of the carbonyl group) forms an enolate anion. **756.** Acetone is brominated in the enol form by the electrophilic addition reaction. **757.** The rate of bromination of acetone is determined by the slow enolization step and does not depend on the bromine concentration or the nature of the halogen. **758.** See answer to Problem 302. **765.** The stability of the hydrate form of the carbonyl compound is the higher, the stronger the accepting properties of the group connected with the carbonyl atom of carbon. (a) $CH_2O > CH_3CHO$; (b) $CH_3CHO < Cl_3CCHO$; (c) $CH_3COCH_3 < CF_3COCF_3$; (d) $HOOC-CHO > H_5C_2OOC-CHO$. **769.** The decreased yields of acetals in the transition from reaction (a) to reaction (b), and also from reaction (c) to reaction (d) is due to steric hindrances. **771.** Hemiacetal of trichloroacetaldehyde is formed easily because of the strong $-I$ effect of the CCl_3 group that facilitates nucleophilic addition of alcohol. A full acetal is formed via the hemiacetal step, and only in conditions of an acid catalysis according to the following:

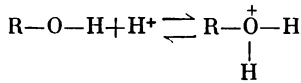


In chloral case, the strong $-I$ effect of the trichloromethyl group ($R = CCl_3$) hinders the formation and dehydration of the product II. **781.** (a) CH_3-CHO; (b) $CH_3-CH=CH-CHO$; (c) $CH_3-CH=CH-CH=CH-CHO$. See answer to Problem 748. **784.** Compounds (a) and (c) can be differentiated by U-V spectroscopy, and compound (b), by I-R spectra. **787.** Protection of the aldehyde group by the conversion of the starting compound into an acetal, the haloform reaction, hydrolysis. **793.** $CH_3COCH_2C(OH)CH_3$ (with CH_3 branch). **795.** Methyl vinyl ketone. **798.** Butyraldehyde. **799.** Diethyl ketone. **812.** Said conversions give carboxylic acid containing one CH_2 group less than in the starting acid (the Barbier-Wieland method). At the second step, the ester of caproic acid reacts with two moles of the Grignard reagent to give a tertiary alcohol which is dehydrated and then oxidized to give valeric acid. **813.** See answer to Problem 812. **844.** The decreasing activity toward the Grignard reagent in the series of acid halides (fluorides, chlorides, bromides) is due to steric hindrances caused by the increasing volume of the halogen atom. **854.** (a) Adding of a mineral acid promotes protonation of the carboxyl group and, as a result,

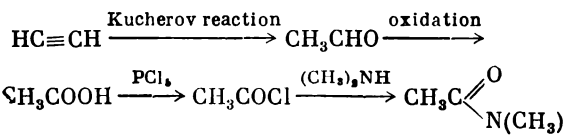
electrophilicity of the carbon of this group increases:



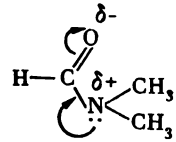
(b) excess mineral acid promotes protonation of not only carboxylic acid, but also alcohol that loses its nucleophilicity in this process:



855. The rate of esterification increases in the series: trimethylacetic, propionic, acetic acids which is due to diminishing steric hindrances.
869. Dimethylacetamide can be obtained according to the following:

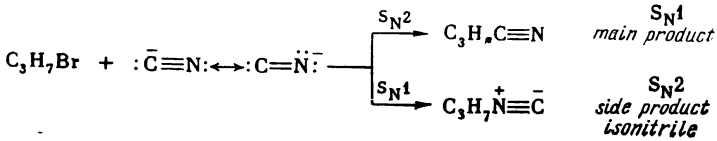


877. Dimethylformamide solvates only cations since the positive end of the dipole in this molecule is shielded by two bulky methyl groups.



Dimethylformamide therefore hinders the S_N1 reactions but accelerates the S_N2 reactions. 878. Cyanide ion CN^-, like nitrite ion NO_2^-, has two nucleophilic centres that are characterized by their basicity:

The direction of the reaction of an alkyl halide with cyanide ion depends (like in the reactions with nitrites) on the mechanism of the reaction. Primary propyl bromide reacts with KCN in an aqueous-alcoholic medium according to the S_N2 mechanism to give a nitrile:



879. (a) The reaction is shifted to the S_N1 side and isonitrile is formed; (b) nucleophilic substitution in dimethylformamide is the S_N2 reaction giving a nitrile. See answers to Problems 607, 877, and 878. **881.** (a) A salt of butyric acid; (b) butylamine; (c) diethylpropylcarbinol; (d) $CH_3CH_2CH_2COOC_2H_5$. **890.** See Appendix, Table 5. **894.** Compounds (a) can be differentiated by their U-V spectra; compounds (b) and (c) by the I-R spectra. See Appendix, Tables 3 and 4. **898.** During electrolysis of a potassium salt of acid malonate ester, diethyl succinate is formed at the anode. (The reaction is similar to synthesis of paraffins by electrolysis of salts of fatty acids.) **899.** By electrolysis of a salt of succinic acid ester with subsequent hydrolysis of the obtained product. **901.** This is explained by that they themselves are sufficiently strong acids (pK_a for HCOOH is 3.75; for oxalic acid pK_a' is 1.23). **905.** (d) $(C_2H_5OOC)_2C{=}NOH$. **907.** $2[CH(COOC_2H_5)_2]^-Na^+ + I_2 \rightarrow (C_2H_5OOC)_2CH{-}CH(COOC_2H_5)_2 + 2NaI$ (c). **910.** Diethyl succinate. **911.** Croton condensation with acetaldehyde, hydrolysis of the obtained ester, decarboxylation. **921.** $(CH_3)_2CH{-}CH(CH_3){-}CH_2COOH$. **923.** Propionic anhydride. **924.** $(CH_3)_2CHCON(CH_3)_2$. **926.** Butyramide. **927.** Butyryl chloride. **928.** Isobutyronitrile. **935.** Ethyl acetate. **940.** Low-selective radical process of substitution (similar to chlorination of alkanes). **943.** (e) Via allyl alcohol. **947.** Ethyl dichloroacetate. **954.** δ-Hydroxy acid, $CH_3{-}CH(OH){-}CH_2{-}CH{=}CH{-}COOH$ is formed. **960.** The characteristic reaction for alpha-hydroxy acids:

$$R{-}CH(OH){-}COOH \xrightarrow[H^+]{H_2O} R{-}CHO + HCOOH$$

985. $(CH_3)_2N{-}CH_2{-}COOC_2H_5$. **986.** alpha-Chloropropionic acid. **987.** alpha-Bromobutyric acid. **996.**

(a) $CH_3{-}\underset{\underset{O}{\|}}{C}{-}\boxed{OCH(CH_3)_2 + H}{-}CH_2{-}\underset{\underset{O}{\|}}{C}{-}OCH(CH_3)_2 \xrightarrow{C_2H_5ONa}$

$$\rightarrow CH_3\underset{\underset{O}{\|}}{C}CH_2COOCH(CH_3)_2 + CH_3\underset{\underset{OH}{|}}{C}HCH_3$$

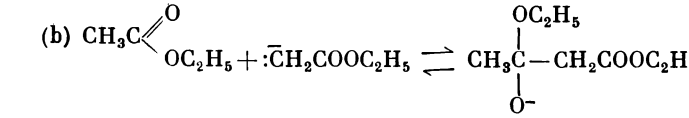
(b) $CH_3CH_2CH_2{-}\underset{\underset{O}{\|}}{C}{-}\boxed{OC_2H_5 + H}{-}\underset{\underset{C_2H_5}{|}}{C}H{-}COOC_2H_5 \xrightarrow{C_2H_5ONa}$

$$\rightarrow CH_3CH_2CH_2{-}\underset{\underset{O}{\|}}{\overset{\overset{C_2H_5}{|}}{C}}{-}CHCOOC_2H_5 + C_2H_5OH$$

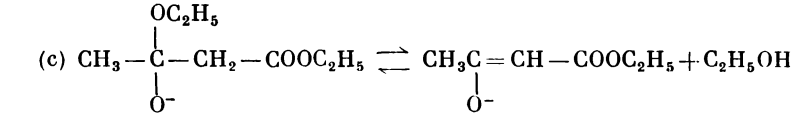
997. Claisen ester condensation is aldol condensation type. First, under the action of a strong base $C_2H_5O^-$, a conjugated anion is formed from a molecule of ethyl acetate:

(a) $C_2H_5O^- + H{-}CH_2COOC_2H_5 \rightleftharpoons :\bar{C}H_2COOC_2H_5 + C_2H_5OH$

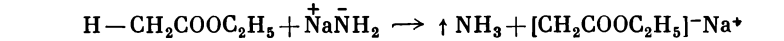
The formed anion (nucleophile) is added to the carbonyl group of the second ester molecule:



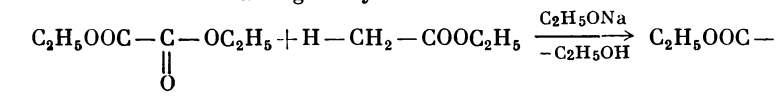
A molecule of alcohol is eliminated from the addition product to give an anion of the enol form of acetoacetic ester:



(1) strong bases, e.g. alkoxides of alkali metals, are used as condensation agents, because the starting esters are weak CH-acids and a strong base can only convert them into anions; (2) despite the fact that all stages are reversible and their equilibria are strongly shifted to the left, reactions (b) and (c) are still realizable since the final product is an energetically advantageous system with conjugated bonds (enolate anion of acetoacetic ester); (3) since all stages of the process are reversible, the yield can be increased by distilling the formed alcohol. It is also possible to make the first stage irreversible by using $NaNH_2$ as a base (taken in equimolecular ratio). Then the ester will all be converted into the anion:

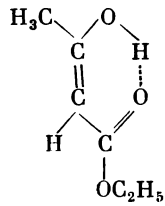


998. A mixture of four esters is formed: (1) acetoacetic ester, (2) methyl acetoacetic ester, (3) propionyl acetic ester, and (4) ethyl alpha-propionylpropionate. See answer to Problem 997. **999.** Esters of oxalic acid have no alpha-methylene group but have $\rangle C{=}O$ groups possessing increased affinity for nucleophilic addition; for this reason the reaction occurs unambiguously:

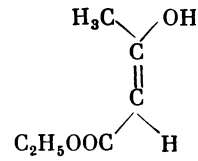


See answer to Problem 997. **1007.** The spectrum of an equilibrium mixture of acetoacetic ester contains the frequency of the keto bond C=O (1715 cm^{-1}), of the ester bond C=O (1740 cm^{-1}), of the chelate bond C=O (1650 cm^{-1}) and conjugated bond C=C (1630 cm^{-1}). As an anion is formed, these frequencies disappear and a frequency of the conjugated system of the anion appears (1662 cm^{-1}). **1012.** Geometric

isomers of the enol form of acetoacetic ester are



cis-



trans-

The *cis*-isomer is more stable because an intramolecular hydrogen bond is formed. **1017.** The resonance signals correspond to the protons of the keto and enol forms of acetylacetone. See Appendix, Table 5. **1023.** The product of O-acylation is formed:

$$CH_3C(OH)=CH-COOC_2H_5+CH_3CH_2COCl \xrightarrow{\text{pyridine}}$$
$$\longrightarrow CH_3C(OCOCH_2CH_3)=CH-COOC_2H_5$$

1024.

(a) $CH_3C(O-CH_2OCH_3)=CH-COOC_2H_5$;

(b) $CH_3C(O-COOC_2H_5)=CH-COOC_2H_5$

In both cases the substitution occurs at the oxygen atom. **1025.**

(a) $CH_3C(=O)-CH(COCH_3)-COOC_2H_5$;

(b) $CH_3C(OCOCH_3)=CH-COOC_2H_5$

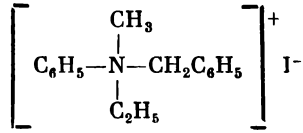
The reaction (a) occurs with the transfer of the reaction centre. **1031.** Diacetyl succinate

$$CH_3CO-CH(CH_3CO-CH-COOC_2H_5)-COOC_2H_5$$

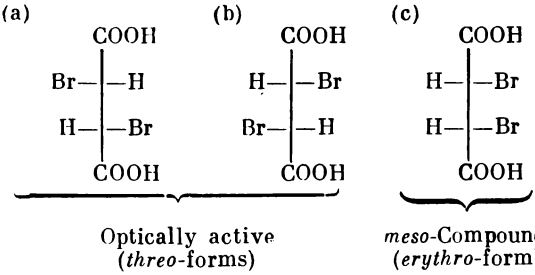
is formed. In the conditions of the ketone cleavage it turns into acetonyl acetone, $CH_3CO-CH_2-CH_2COCH_3$. **1032.**

$$C_2H_5OOC-CH(CH_2)CH-COOC_2H_5 \xrightarrow[(H^+,\ heat)]{H_2O}$$
$$C_2H_5OOC-CO \qquad CO-COOC_2H_5$$
$$\longrightarrow HOOC-CO-CH_2-CH_2-CH_2-CO-COOH+4C_2H_5OH+2CO_2$$

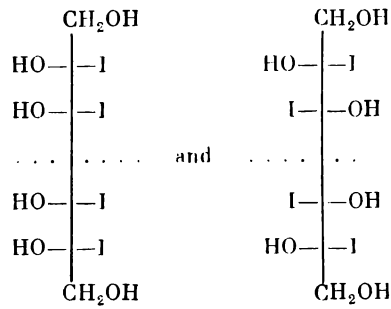
1037. (a) Succinic acid; (b) $CH_3COCH_2CH_2COCH_3$. **1041.** $CH_3CH_2COCH(CH_3)—COOC_2H_5$. **1046.** (a) Optical activity is observed in quaternary ammonium compounds having tetrahedral structure, e.g. in the salt:



1056.

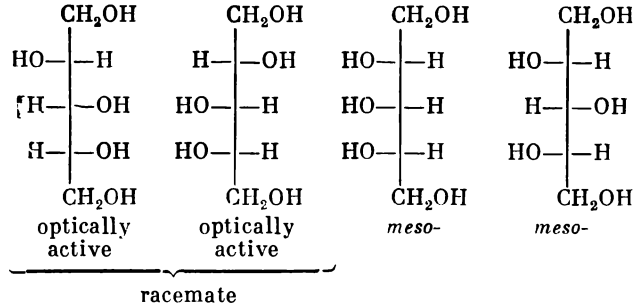


1059. Optically inactive isomers (*meso*-forms) are observed in compounds (a) and (c). In the case with (b) there are two *meso*-forms:

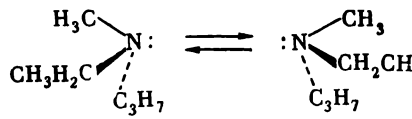


1062. In the given compound the carbon atoms 2 and 4 are usual centres of asymmetry. The carbon atom 3 is pseudoasymmetric, i.e. its properties of symmetry depend on the configuration of the atoms 2 and 4. If the configurations of the second and fourth carbon atoms are different, the 3rd carbon atom becomes asymmetric and the existence of a pair of enantiomers and a racemic compound becomes possible. If the 2nd and the 4th carbon atoms have the same configu-

ration, two *meso*-forms are possible:



1065. Nitrogen of this tertiary amine is an asymmetric centre, but the rapid interconversion of the enantiomers makes it impossible to observe optical activity:



1064. See answer to Problem 1046. **1066.** The D-series comprises compounds (a), (c) and (e); the L-series comprises (b), (d) and (f). **1069.** Monomethyl ester of mesotartaric acid. **1074.** *trans*-2-Butene forms *meso*-2,3-dibromobutane, and *cis*-2-butene gives the racemic compound of *threo*-forms of 2,3-dibromobutane. **1075.** Fumaric acid gives *meso*-2,3-dibromosuccinic acid, and maleic acid gives the racemic compound of *threo*-forms of 2,3-dibromosuccinic acid. **1076.** *cis*-Isomer forms the racemic compound of *threo*-forms of 2,3-dibromobutyric acid, and *trans*-isomer gives the racemic compound of *erythro*-forms of the same acid. **1083.** A deeper racemization is observed with the compound (b) since a stabler intermediate tertiary carbonium ion is formed here. **1084.** See answer to Problem 1083. **1086.** *meso*-Compound is formed. **1087.** (a) Inversion of configuration (S_N2 mechanism); (b) retention of configuration (S_Ni mechanism). **1088.** Via L-2-chlorobutane using nucleophilic substitution reactions (S_Ni and S_N2 reactions).

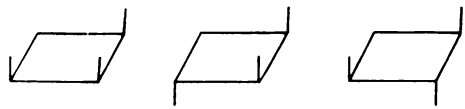
1089. (b) D-2-chlorobutane $\xrightarrow[S_N2]{KOH}$ L-2-butanol $\rightarrow$

$\xrightarrow[S_Ni]{SOCl_2}$ L-2-chlorobutane $\xrightarrow[S_N2]{KOH}$ D-2-butanol;

(c) L-2-bromobutane $\xrightarrow[S_N2]{KOH}$ D-2-butanol $\xrightarrow{SOCl_2}$ D-2-chlorobutane.

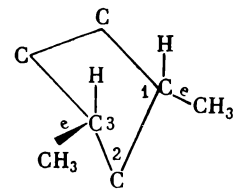
1090. (a) Retention of configuration (double inversion); (b) and (c) inversion of configuration. **1091.** (b) Retention of configuration

(double inversion); (c) inversion of configuration. **1093.** Mesotartaric acid. **1095.** The loss of optical activity is due to spontaneous enolization of the acid that causes racemization. **1104.** (a) 1-Methyl-3-ethylcyclobutane (*cis*- and *trans*-); (b) 1-methyl-2-ethylcyclobutane (*cis*- and *trans*-isomers, each in the form of a pair of enantiomers). **1110.** Three configurations:



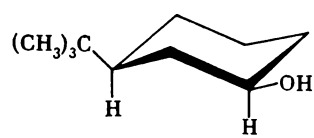
cis, cis- *cis,trans-* *trans, trans-*

1111. (c) *cis*-Isomer is about 2.09 kJ/mole more stable. The envelope model can help understanding: if the carbon atom C_2 is outside the plane of the carbon atoms C_1 and C_3 (connected by methyl groups), *cis*-methyl groups can assume positions similar to the equatorial positions of cyclohexane:

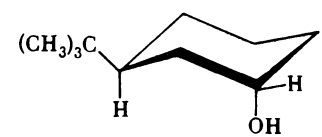


In the *trans*-isomer, only one methyl group can assume this advantageous position. **1114.** *trans*-1,2-Dibromocyclohexane (*e,e*). **1115.** Conformations *a,a* and *e,e*. The latter is more stable since because of the repulsion, the substituents will assume the farthest positions from each other. **1116.** For 1,3-dimethylcyclohexane (*e,e* conformation).

1117.



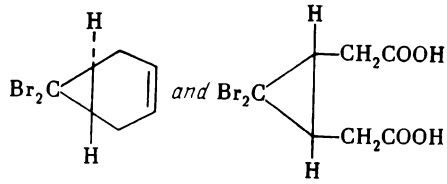
cis-(e,e)



trans-(e,a)

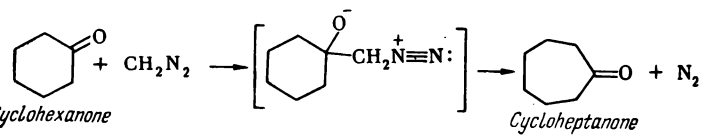
1118. *trans*-1,2-Dibromocyclohexane predominates in the diequatorial conformation since the dipole moment for the diaxial isomer can be considered zero. **1120.** *cis*-Decalin is formed in the former case and *trans*-decalin in the latter. *trans*-Decalin is a more stable isomer since the rings are closed across two equatorial bonds. **1123.** Spirocyclopen-

tane **1127.** Via ethyl adipate and ethyl 1,2-cyclopentanonecarbonate. **1130.** (a) Product of the Dieckmann condensation; (b) product of acyloin condensation. **1131.** 1,1-Dichlorotetramethylcyclopropane that forms by electrophilic addition of dichlorocarbene across the double bond. **1132.**



I II

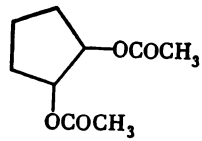
1133. 1,1,2,2-Tetrachloro-3,3,4,4-tetrafluorocyclobutane. **1135.** Use (a) divinyl and acrolein; (b) divinyl and maleic anhydride; (c) 2,4-hexadiene and acrylic acid as dienes and dienophiles, respectively. **1141.** Double bond is broken with the formation of the corresponding glycol. A three-membered ring is more stable to oxidating agents and remains so in the given conditions. **1149.** (a) With equatorial OH group; (b) with axial OH group. Ester with equatorial acetoxy group is easier to hydrolyze. **1151.** Cyclobutanone is more reactive in nucleophilic addition since the change in the character of hybridization ($sp^2 \rightarrow sp^3$) decreases the angle strain since the angle of 90° is closer to the tetrahedral angle (109°28′) than to the trigonal angle (120°). In five-membered rings, predominates the strain of the eclipsing bonds (Pitzer strain), the $sp^2 \rightarrow sp^3$ transition in cyclopentanone increases this strain. **1152.** In cyclohexanone, the change from sp^2 to sp^3 hybridization results in the formation of the chair conformation, free from the Pitzer strain. (See also answer to Problem 1151.) **1155.** Cyclohexanone can be separated in the form of a crystalline bisulphite derivative from which ketone is recovered by treatment with soda solution on heating. **1157.** This reaction widens the ketone ring:



Cyclohexanone *Cycloheptanone*

1165. The starting compound is beta-keto ester, and like acetoacetic ester it can be used to synthesize ketones (ketone cleavage). **1166.** An equilibrium mixture of cyclohexane and methylcyclopentane is formed in both cases. This indicates that five- and six-membered rings

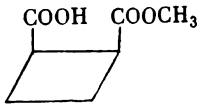
are almost equally stable. **1167.** In the absence of water, cyclopentanecarboxylic acid is formed (Favorsky rearrangement). In the presence of water, the hydroxy group is substituted for chlorine atom (nucleophilic substitution). **1168.** Deamination accompanied by the Demyanov rearrangement takes place. **1169.** See answer to Problem 1168. **1170.** See answer to Problem 1168. **1179.** Electrophilic addition of water, via the intermediate formation of a carbonium ion, gives a mixture of

cis- and *trans*-1,2-dimethylcyclohexanols. **1180.** 

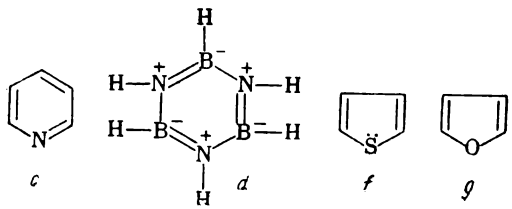
(1,2-diacetoxycyclopentane). **1181.** In reactions (d), (e) and (f) diene synthesis occurs. **1182.** Cyclopentadienylpotassium and cyclopentadienylmagnesium bromide. The activity of the hydrogen atom of the methylene group of cyclopentadiene is explained by the formation

of a stable aromatic cyclopentadienyl anion: **1184.** Cycloal-

kynes are formed readily provided the ring contains 13 or more carbon atoms, i.e. if the linear system —C≡C— can be formed without strain. The simplest known cycloalkyne is cyclooctyne, but its molecule is under a strain. **1185.** Cyclopentane (I), 2-pentene (II). **1186.** 1,2,3-Trimethylcyclopropane. **1188.** 5-Ethylcycloheptene. **1189.** *trans*-1,3-Dimethylcyclobutane. **1191.** *trans*-2-Methylcyclopropanecarboxylic acid. It exists as two enantiomers. **1192.** Cyclohexanone. **1193.** 3-Methylcyclopentanone. **1194.** $CH_3-(CH_2)_7-\underset{\diagup\ \diagdown}{\overset{CH_2}{C}}=C-(CH_2)_7-COOH$. **1195.** Racemic *trans*-1,2-cyclopropanedicarboxylic acid.

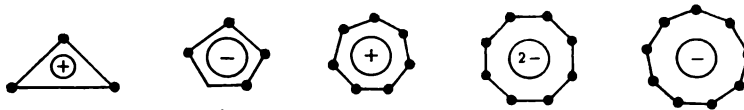
1196. 

1197. Cyclooctane.

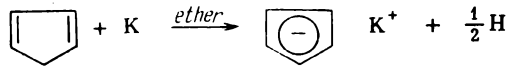
1208. 

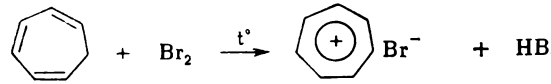
These com-

pounds obey the Hückel rule, n being 1. **1211.** The following ions have aromatic character:



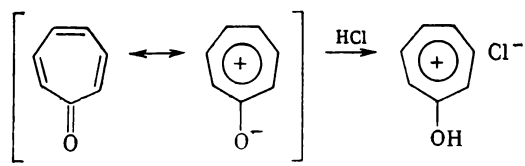
a *b* *c* *d* *e*

1212. *(a)* 

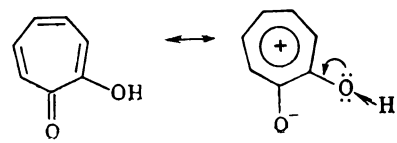
(b) 

1214. Relatively high dipole moments in fulvene and tropone depend on the considerable contribution from the structures containing aromatic ions:

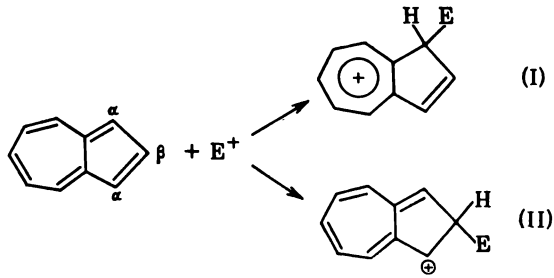
1215. Tropylium bromide

1216. 

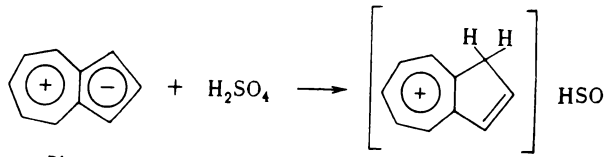
1217. Acid properties of tropolone depend on its aromaticity:



1218. Electrophilic substitution occurs at the alpha-position of the five-membered ring, since this gives the most stable cation (I):



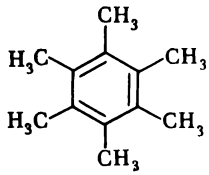
1219.



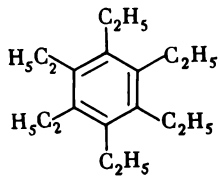
Blue *Colourless*

1225. The first stage, consisting in the action of electrophilic reagent Br^+, is similar to ethylene and benzene: the corresponding carbonium ion is formed in each case. The main difference between aromatic substitution and electrophilic addition to alkenes consists in the course of the second stage. σ-Complex is stabilized by ejection of H^+ since an aromatic compound is thus formed, which is advantageous from the energy view point. The carbonium ion formed from ethylene reacts with the nucleophilic reagent since this envolves deprotonization—the process that is less advantageous from the energy view point. **1235.** The partial rate factor, *f*, defines the relative activity of a definite position (*o*-, *m*-, *p*-) in a substituted benzene compared with benzene. **1240.** The negative inductive effect increases from H to Br, Cl and F, and this increases the inactivating action of substituents in the *ortho*- and *para*-positions. This decreases also selectivity of substitution and increases the yield of *meta*-isomer. **1241.** As the nitro group is removed from the aromatic nucleus, its deactivating action decreases. The nitro group in nitrobenzene is a strong *meta*-director, but in 1-nitro-2-phenylethane the substituent turns into *ortho*-, *para*-director. **1243.** In our reactions, electrophilicity of the substituent increases and the selectivity of substitution decreases. **1244.** The amount of the *ortho*-isomer decreases since the volume of the alkyl substituent available increases (effect of the spatial factor). **1245.** The ratio of *ortho*- to *para*-isomers depends on the volume of the entering substituent. The bulky bromine atom makes the *ortho*-substitution difficult. **1246.** Owing to spatial effect of methyl groups, the amino group is freed from conjuga-

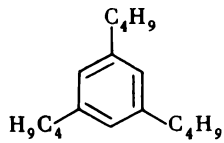
tion with the nucleus; the negative inductive effect of acetamino group inactivates the nucleus. **1257.** *o*-Xylene and ethylbenzene. **1258.** Cyclopentane will not change, and cyclohexane will turn into benzene. **1260.** Low-temperature cyclotrimerization of acetylene hydrocarbons is accomplished in the presence of nickel carbonyl $[Ni(CO)_2]$:



a

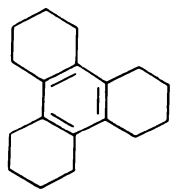


b



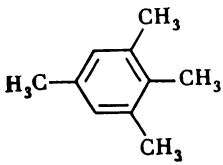
c

1261. (b) 1,3,5-Triphenylbenzene, (c)

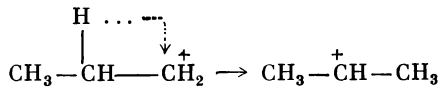


c

1267. Isodurol,

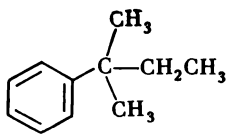


1271. Under the influence of $AlCl_3$, *n*-propylcarbonium ion $CH_3CH_2CH_2^+[AlCl_4]^-$ is formed, which is isomerized by the hydride transfer into a more stable isopropyl cation



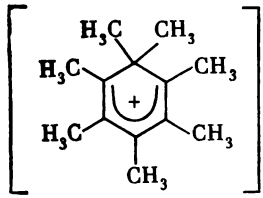
The latter alkylates benzene to give isopropylbenzene.

1272.

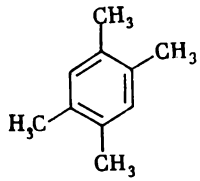


1273. As the volume of the halogen

atom increases, the formation of the complex with the catalyst becomes more difficult. **1275.** Stability of this salt

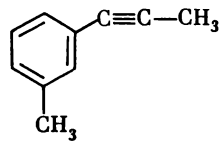


$AlCl_4^-$ is explained by the stabilizing action of methyl groups due to their positive inductive effect. **1277.** Cyclohexylbenzene is formed in all cases. **1278.** Durol,



1279. (a) $C_6H_6 + CH_2{=}CH_2 \xrightarrow{H_3PO_4} C_6H_5CH_2CH_3$

$\xrightarrow[500°C]{Cr-Al_2O_3} C_6H_5CH{=}CH_2$, (b) as in the previous case. **1291.** The end product is *tert*-butylbenzoic acid. **1301.** Sodium salt of phenylacetic acid. **1305.** 1,2,3-Trimethylbenzene, 1,2,4-trimethylbenzene and *o*-xylene. **1308.**



1309. Two compounds:

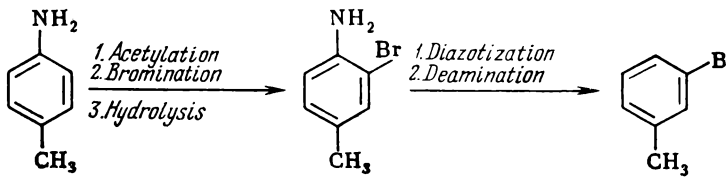
(1) $C_6H_5{-}C(CH_3){=}CH_2$ and (2) $C_6H_5CH{=}CH{-}CH_3$

1310. Isopropylbenzene. **1317.** The mechanism of benzene iodination in the presence of Ag_2SO_4 has the character of electrophilic substitution:

$$Ag^+ + I_2 \longrightarrow AgI + I^+ \qquad C_6H_6 + I^+ \longrightarrow C_6H_5I + H^+$$

1322. 1,2,4,5-Tetrachlorobenzene.

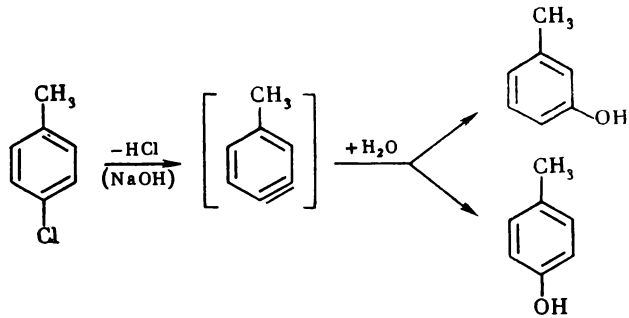
1324.



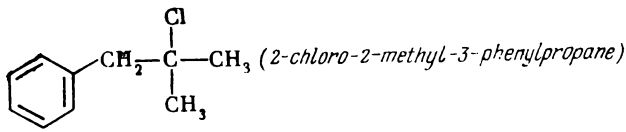
1330. The Blanc chloromethylation:

$$ArH+HC\overset{O}{\underset{H}{<}}+HCl \xrightarrow[60°]{ZnCl_2} ArCH_2Cl+H_2O$$

1331. Chloromethylation of *p*-xylene. (See answer to Problem 1330). **1336.** The reaction proceeds with the intermediate formation of a compound of the dehydrobenzene type. Further addition of a nucleophile can proceed in two ways, e.g. in the case (a)



1346. *m*-Ethylbenzoic acid. **1363.**

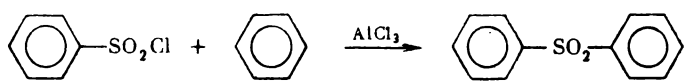


(2-chloro-2-methyl-3-phenylpropane)

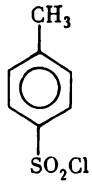
1368. The rate of nitration is determined by the slow step at which σ-complex is formed. The second stage (break-down of the C—H bond) occurs rapidly. Replacement of the hydrogen atom by the atom of deuterium does not produce any effect on the rate of nitration. During sulphonation, the rate-limiting step is elimination of the proton from the σ-complex. **1373.** Sulphonation is a reversible reaction and the character of the reaction products is therefore controlled thermodynamically. At 100°C *para*-isomer is more stable. **1383.** Methyl groups stabilize σ-complex of electrophilic substitution. **1386.**

(a) $C_6H_5SO_2Cl \xrightarrow[0°C]{Zn;\ HCl} C_6H_5SH$

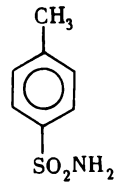
Thiophenol

(*b*) 

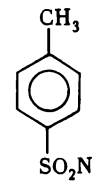
1388. The stronger electron-accepting character of the SO_2 grouping (compared with the carbonyl) accounts for the strongly acid character of sulphamides. They readily form salts with alkali metals, e.g. $C_6H_5SO_2NHNa$. **1390.**



I

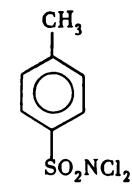


II



Chloramine-T

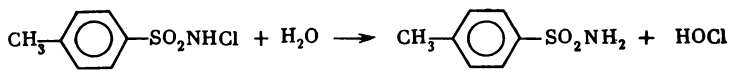
III



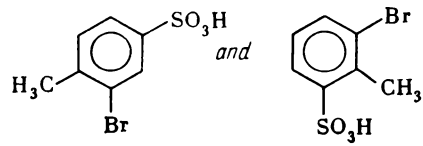
Dichloramine-T

IV

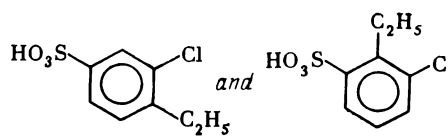
Compounds III and IV slowly liberate hypochlorous acid in the presence of water and are therefore effective antiseptics:



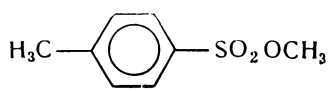
1395. Carry out successively: sulphonation, bromination, desulphonation. **1396.** Carry out successively: sulphonation, nitration, acid hydrolysis. **1400.**



1401.

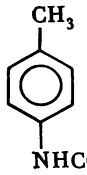
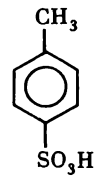


1402.



1407. Because of the increasing concentration of the nitrating agent NO_2^+. **1408.** The nitro group has a much stronger deactivating action than the sulpho group. **1409.** (a) Dilute nitric acid; (b) and (c) concen-

trated (68 per cent) nitric acid and concentrated sulphuric acid; (d) and (e) KNO_3 and concentrated sulphuric acid. **1434.**

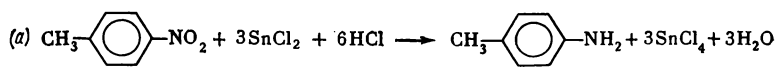
(a) via  ; *(b) via* 

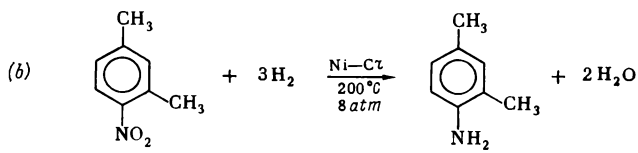
1436.

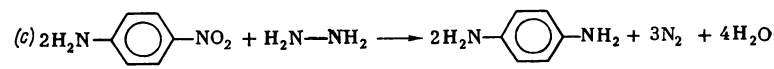
(a) $C_6H_5NHOH+2[Zn(NH_3)_2]Cl_2+H_2O$

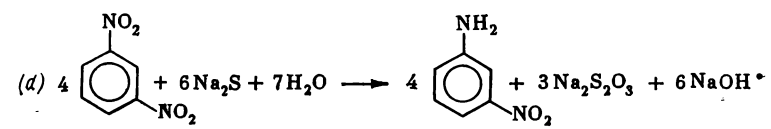
(b) $2C_6H_5-N=N-C_6H_5+3HCOONa+3H_2O$ (with $\downarrow O$)

1441. *o*-Nitroaniline. **1442.** *m*-Nitrochlorobenzene. **1445.** 2,4- and 2,6-dinitrotoluenes. **1446.** 3,5-Dinitrobenzenesulphonic acid. **1454.**

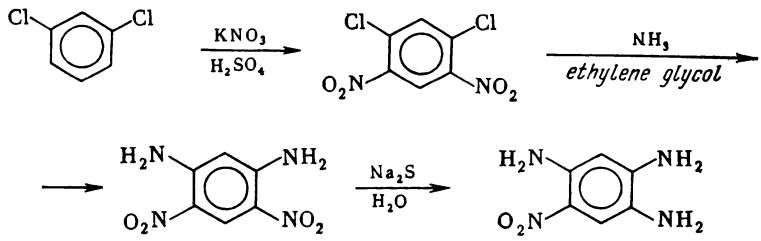
(a) 

(b) 

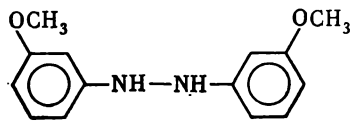
(c) 

(d) 

1458.

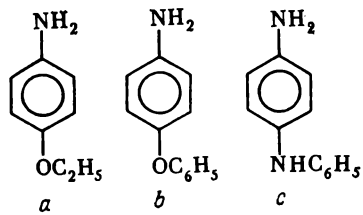


1464. Conjugation of the amino group with aromatic nucleus decreases the electron density on the nitrogen atom and increases electron densities in *ortho*- and *para*-positions. **1491.** Direct nitration of aniline gives a mixture of *m*- and *p*-nitroanilines and appreciable resinification. For this reason, *m*-nitroaniline is obtained by partial reduction ($Na_2S + H_2O$) of *m*-dinitrobenzene. **1492.** Dimethylamino group in an acid medium is protonated and becomes the second type director. **1497.** Accomplish the following steps: acylation, bromination, hydrolysis. **1499.** Use the Hofmann rearrangement of β-phenylpropionic amide. **1503.**



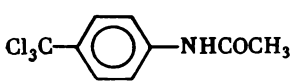
1506. The intermolecular electrophilic rearrangement is accompanied by isomerization of the primary carbonium ion into a more stable tertiary one.

1509.

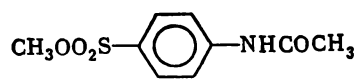


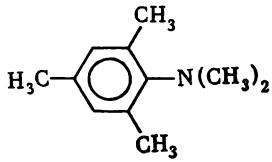
Intermolecular nucleophilic rearrangement. **1510.** N-Nitrosation and the rearrangement into C-nitroso compound. **1511.** Dimethylaniline. **1512.** Dimethylaniline. **1514.** Benzylamine. **1515.** The I-R spectrum corresponds to acetanilide.

1516.

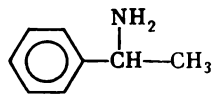


1517.

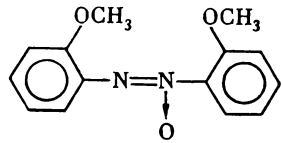


1518. 

1519. *p*-Nitroacetanilide.

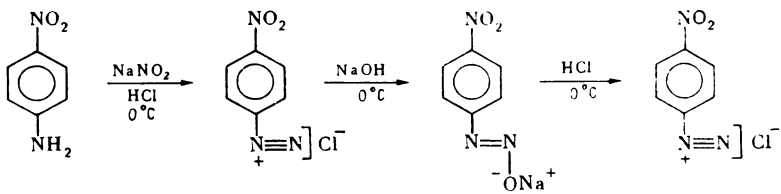
1520. 

1521. Hydrazobenzene.

1522. 

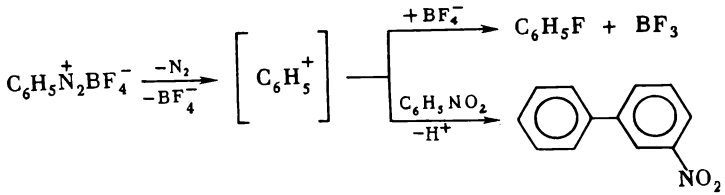
1530. (a) *p*-Toluidine is diazotized in an aqueous solution in the cold to give nitrous acid from sodium nitrite by adding a mineral acid; (b) weakly basic 2,4,6-trinitroaniline is diazotized with concentrated sulphuric, phosphoric or acetic acid.

1538.

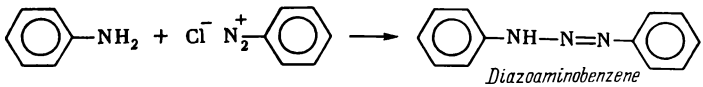


1541. For compounds (a) and (c), the method of alkaline fusion of salts of the corresponding sulphonic acids is inapplicable since nitro compounds and halogen derivatives are sensitive to the action of alkalis at high temperatures. **1543.** This is the S_N1 reaction. In an aqueous-methanol medium, the competing nucleophiles are molecules of water and methyl alcohol. **1544.** Substitute the methoxy group for the chlorine atom, then reduce, diazotize, and decompose the diazonium salt in an aqueous medium. **1547.** The formation of 3-nitrodiphenyl alongside with fluorobenzene is the result of an electrophilic attack on

nitrobenzene by phenyl cation:

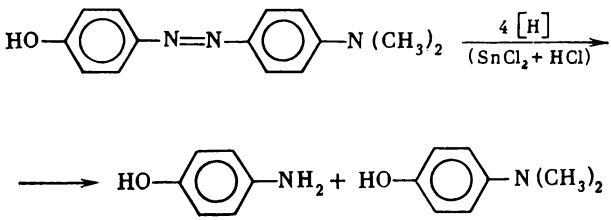


1555. Act as follows: nitrate, chlorinate, reduce, diazotize, and substitute iodine for the diazonium group. **1557.** The competing reactions are deamination and replacement of the diazonium group by the alkoxy group. **1559.** Act as follows: reduce, brominate, and deaminate. **1563.**



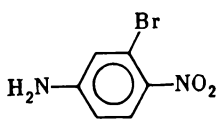
Diazoaminobenzene

1573. Diazoaminobenzene; *p*-aminoazobenzene. **1575.** Electrophilicity of the diazonium cation depends on the magnitude of the positive charge on the extreme nitrogen atom ($Ar-\overset{\cdots\cdots}{\overset{+}{N}}\equiv N:$); it decreases in the series: (c) > (a) > (b). **1576.** 2,4,6-Trinitrophenyldiazonium cation has high electrophilicity owing to the strong electron-accepting character of the nitro groups. **1586.** To establish the structure of azo dyes, reducing splitting is often used:

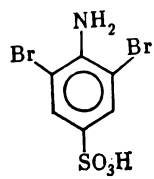


1588. See answer to Problem 1586. **1591.** *p*-Aminophenylnitromethane. **1592.** Dimethylaniline. **1593.** *p*-Nitrobenzylamine.

1595.

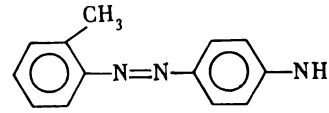


1596.

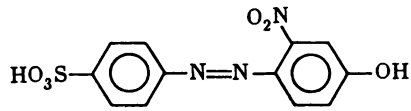


1597. Diazo-

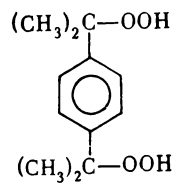
aminobenzene. **1599.**



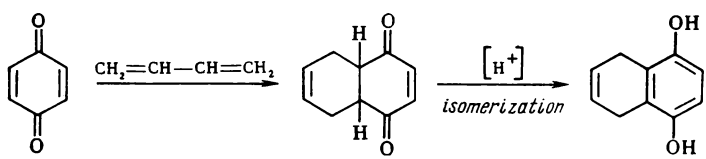
1600.



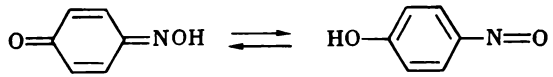
1613. In 2,4-dinitrophenol, the electron-accepting nitro groups stabilize the acid anion. **1617.** The conjugation of the phenol hydroxyl with the aromatic nucleus weakens the nucleophilic character of phenol. It can therefore be acylated only by strong agents such as acid anhydrides and halides. **1618.** Conjugation of the phenol hydroxyl with the aromatic nucleus hinders nucleophilic substitution of bromine for the OH group. **1619.** *o*- and *p*-Hydroxyacetophenones. **1623.** Sulphonation is a reversible reaction. At low temperature the kinetic control gives a faster substitution in the *ortho*-position. At 100°C, the main reaction product is the *para*-isomer, which is more stable (thermodynamic control). **1629.** A good yield of *p*-nitrophenol free from the *ortho*-isomer is obtained via *p*-nitrosophenol by oxidizing it with dilute nitric acid. **1632.** The sulphonation reaction is reversible and the nitro groups are therefore readily substituted for the sulpho groups. **1633.** The nitro group in the *meta*-position to the OH group shows a negative inductive effect. In the *para*-position a negative mesomeric effect is added. See also answer to Problem 1613. **1640.** Picric acid is the end product. **1647.** Dihydroperoxide of *p*-diisopropylbenzene:



1660. (c) > (b) > (a). **1663.**

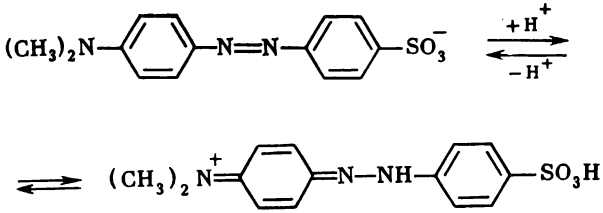


1664. The products of both reactions are connected by the tautomeric conversion:

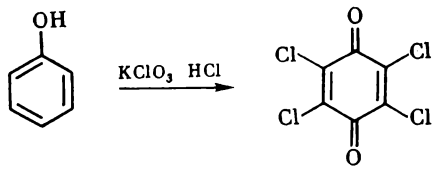


Quinone monoxime *p-Nitrosophenol*

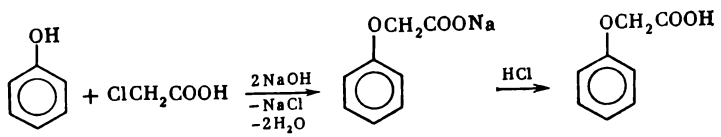
1665.



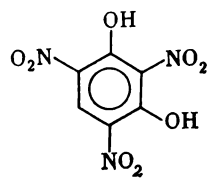
1666.



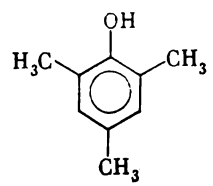
1684. *p*-Propylphenol and *p*-isopropylphenol. **1685.** Phenoxyacetic acid. It is obtained by slowly adding an aqueous solution of alkali to molten phenol in monochloroacetic acid:



1686.

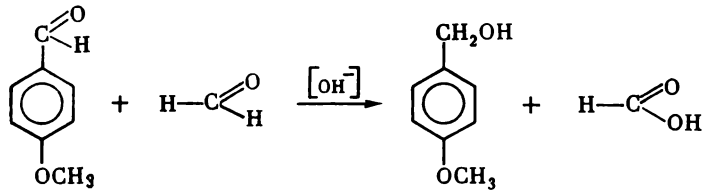


1687. Anisole. **1688.**

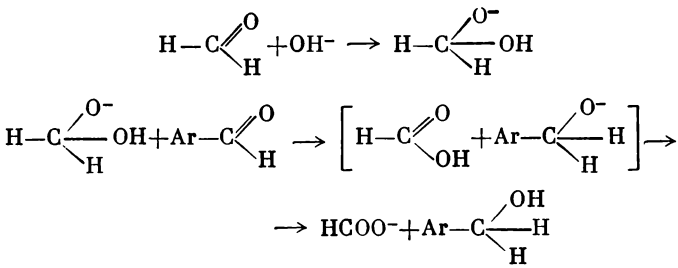


1689. Benzyl alcohol. **1690.** *p*-Benzoquinone monooxime. **1691.** Chloranil (tetrachloro-*p*-benzoquinone). **1699.** Nitro groups activate the methyl group so strongly that it can be condensed with *p*-nitroso-

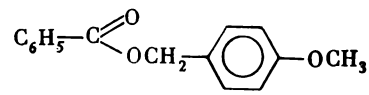
N,N-dimethylaniline. 2,4,6-Trimethylbenzaldehyde cannot be obtained by this method. **1701.** Formyl fluoride reacts with aromatic hydrocarbons in the presence of BF_3 with the formation of aldehydes. This is the S_N2 (aromatic) reaction. **1703.** *p*-Hydroxybenzaldehyde is obtained as a side product. The main reaction product is separated from it by steam distillation. **1708.** Act as follows: nitrate, reduce, diazotize, and replace the diazonium group by the hydroxyl. **1709.** Carry out the following reactions: Reimer-Tiemann reaction, nitration, reduction with sodium sulphide. **1716.** The methyl group (first-type substituent) facilitates further electrophilic substitution; the acetyl group (second-type substituent) makes the subsequent substitution difficult. **1719.** Nitro compounds cannot be acylated by the Friedel-Crafts reaction. For this reason (c) can, and (a) and (d) cannot be obtained by this reaction. In the case with (b) it can be obtained only from benzene and *m*-nitrobenzoyl chloride. **1720.** Through ethyl phenyl ketone. **1740.** In the cross Cannizzaro reaction, the oxidation-reduction process occurs between different aldehydes one of which is formaldehyde, for example

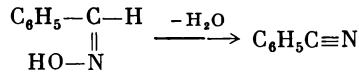


Since formaldehyde is more reactive, it adds the hydroxyl ion and then gives off one of the two hydrogens in the form of the hydride ion to the less active aldehyde:

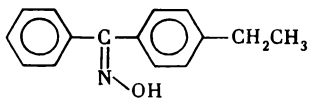


1741. See answer to Problem 1740. **1742.** The following compounds are formed:

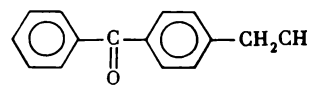
1743. The end product is  **1749.** The end product is ω-nitrostyrene. **1750.** (a) Condense benzaldehyde with malonic ester and then hydrolyze, decarboxylate, and reduce; (b) condense benzaldehyde with malonic ester and then hydrolyze, decarboxylate, and finally add ammonia. **1762.** anti-Benzaldoxime is easier to dehydrate (*trans*-elimination):



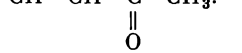
1766.

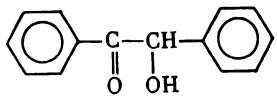


Oxime

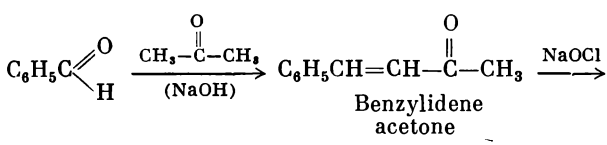


Ketone

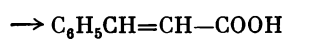
1777. *p*-Bromoacetophenone. **1778.** 

1781.  **1782.** *p*-Chlorobenzaldehyde. **1793.** Acetylation by the Friedel-Crafts method with subsequent oxidation with hypobromite. **1794.** (b) Acetylation of 1,2,4-trimethylbenzene by the Friedel-Crafts reaction, the haloform reaction, oxidation with $KMnO_4$. **1805.** Through cinnamaldehyde and the product of its condensation with acetic anhydride by the Perkin reaction.

1806.



Benzylidene acetone



1808. (a) Resorcinol; (b) hydroquinone; (c) *m*-aminophenol. **1812.** (c) Bromination into the ring, oxidation to aldehyde, condensation

with acetic anhydride, and reduction. **1826.** The I-R spectrum given in Fig. 56 belongs to *p*-toluic acid amide. **1829.** During esterification the nucleophilic reagent (alcohol) attacks the sterically hindered carbon atom of the carboxyl group. During alkylation of a silver salt, the acid anion reacts with the carbon atom of methyl iodide. **1830.** *ortho*-Methyl groups of mesitylenecarboxylic acid produce a blocking action (spatial factor effect). **1832.** Benzoyl chloride is less reactive since because of the conjugation of pi-electrons of the nucleus with the pi-electrons of the carbonyl group, the electrophilicity of the carbon atom of the carbonyl group is lowered. **1848.** The end products are:

and $NH_2CH_2CH_2OH$ **1850.** In *cis*-isomer, the COOH group deviates from the position coplanar with the double bond because of the compression from the adjacent group C_6H_5 that destroys conjugation between the given groups and increases acidity. **1862.** Racemic acid, $C_6H_5CH(OH)COOH$. **1863.** Phenylacetic acid amide. **1865.** *o*-Nitrobenzoic acid amide. **1866.** *p*-Bromobenzoic acid. **1867.** Methyl cinnamate. **1873.** (1) A substituent (or substituents) in the *ortho*-position should be sufficiently bulky to interfere with the free rotation around the C—C bond; (2) each nucleus should be substituted asymmetrically. **1874.** Compounds (b) and (d) are split. In compounds (a) and (c) the asymmetry is absent. **1875.** See answer to Problem 1873. **1880.** Heating acetophenone in a sealed tube in the presence of hydrochloric acid. **1885.**

$$\underset{\text{Colourless}}{(C_6H_5)_3C{-}OH} \overset{+H^+}{\rightleftharpoons} (C_6H_5)_3C{-}\overset{+}{O}H_2 \overset{(-H_2O)}{\rightleftharpoons} \underset{\text{Yellow}}{(C_6H_5)_3C^+}$$

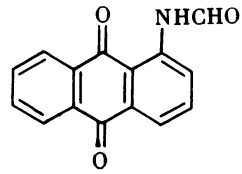
The motive force of the reaction is the formation of a stable carbonium ion. **1886.** A stable triphenylmethyl carbonium ion is formed in a solution of liquid sulphur dioxide:

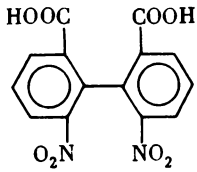
$$\underset{\text{(colourless ether)}}{(C_6H_5)_3C{-}Cl} \overset{SO_2,\ 0^\circ}{\rightleftharpoons} \underset{\text{(yellow)}}{(C_6H_5)_3C^+ + Cl^-}$$

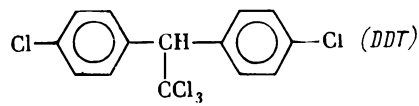
1887.
$$\underset{\text{(colourless)}}{(C_6H_5)_3CH} + NaNH_2 \rightleftharpoons \underset{\text{(red)}}{(C_6H_5)_3C^- : Na^+} + NH_3$$

1894. Diphenylacetylene. **1902.** Nitration. **1905.** Unlike nitration, sulphonation is a reversible reaction. At lower temperature, the kinetic control gives alpha-sulphonic acid. At higher temperatures a more

stable beta-isomer is formed (thermodynamic control). **1907.** (1) Na + alcohol; (2) H_2—Ni (140°C, 30 atm); (3) H_2—Ni (200°, 100-300 atm). The last step is the most difficult to occur since the aromatic system of the benzene ring breaks. **1909.** Only one naphthalene nucleus reacts with two moles of ozone to give glyoxal and phthalic aldehyde. **1924.** 2-Hydroxynaphthoic acid. **1935.** The end product is

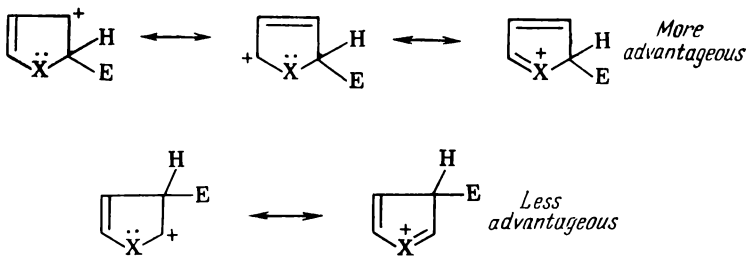
1-(formylamino)-anthraquinone, 

1937. Diphenylcarbinol (benzhydrol). **1938.** 

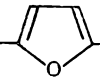
1940. N-Phenyl-β-naphthylamine. **1943.** 

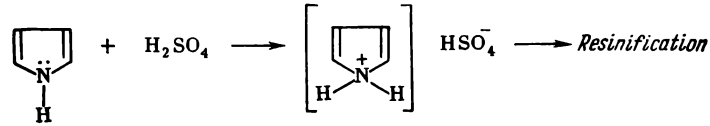
(DDT)

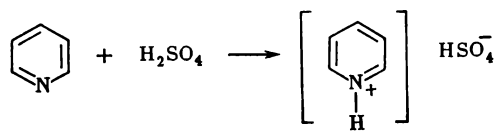
1950. Acrolein → acrolein diacetate → 4,4-diacetoxybutanal → succinic aldehyde → thiophene. **1959.** The direction of electrophilic substitution is determined by the formation of the most stable σ-complex. During substitution in alpha-position, the positive charge is deeper delocalized:



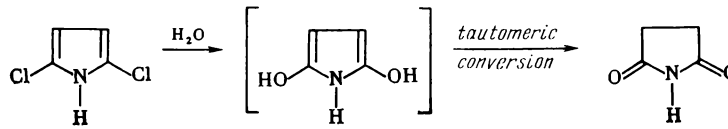
1964. In all cases the Friedel-Crafts acylation is used.

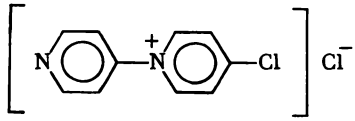
1966.  **1968.** (a) Condensation of the croton type with propionaldehyde; (b) the Perkin reaction with propionic anhydride. **1977.** Indole. **1978.** (a) 5,7-Dinitro-2,3-dimethylindole; (b) 5-nitro-2-methylindole; (c) 1,2,3,4-tetrahydrocarbazole. **1979.** 3-Acetylindole. **1980.** All compounds have a weakly acid character, which slightly increases during transition from pyrrole to indole and then to carbazole because of the increasing conjugation of the pair of electrons of nitrogen with the aromatic nuclei. **1982.** Lower basicity of pyridine, compared with trimethylamine, is due to the difference in hybridization of the nitrogen atom in these compounds (sp^2 in pyridine and sp^3 in trimethylamine).
1985.



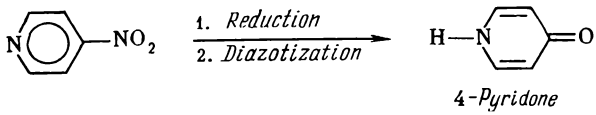


The resinification of pyrrole is due to destruction of the aromatic character of the ring. **1988.** Through pyridine N-oxide. **1990.** (c) α-Methylpyridine is formed. **1991.** (b) The first method: via beta-nitropyridine with subsequent reduction, diazotization, replacement of the diazonium group by the CN group, and hydrolysis. Another way is through beta-pyridinesulphonic acid by fusing it with KCN and subsequent hydrolysis of nitrile. **1992.** α- and γ-Chloropyridines have greater affinity for nucleophilic substitution reactions than beta-isomers (analogy with isomeric nitrohalogenbenzenes). **1993.** Stable diazo compound is formed by 3-aminopyridine.
2000.



2001. 8-Ethylquinoline. **2002.** 

2003.



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APPENDIX

Table 1

Dissociation Energy of Bonds in Molecules of Some Organic and Inorganic Compounds

Bond	$E_{diss.}$, kJ/mole	Bond	$E_{diss.}$, kJ/mole	Bond	$E_{diss.}$, kJ/mole
CH_3-CH_3	347.50	CH_3-H	427.05	H—F	560.22
CH_3-F	494.04	F—F	159.10	H—Cl	431.24
CH_3-Cl	334.94	Cl—Cl	242.83	H—Br	368.44
CH_3-Br	280.52	Br—Br	192.59	H—I	297.26
CH_3-I	221.90	I—I	150.72		

Table 2

Energies of Some Bonds

Bond	Energy, kJ/mole
C=C	613.37
C=O	741.06
C—O	355.89
O—H	460.57
C—H	412.31

Table 3

Characteristics of Simple Chromophore Groups (U-V Region)

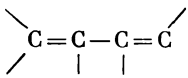
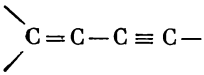
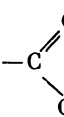
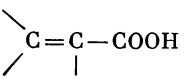
Chromophore group	Compound	λ_{max}, nm	ε_{max}, l/mole·cm	Solvent
	Ethylene	171	15 530	—
	1,3-Butadiene	217	20 900	*n*-Hexane
	2-Octyne	178 196 223	10 000 2 100 160	*n*-Heptane ditto ditto
	Vinylacetylene	219 228	7 600 7 800	*n*-Hexane ditto
	Acetaldehyde	160 180 290	20 000 10 000 17	Vapours ditto ditto
	Acetone	166 189 279	16 000 900 15	ditto *n*-Hexane ditto
	Crotonaldehyde	218 320	18 000 30	Ethanol ditto
	Acetic acid	208	32	ditto
	*cis*-Crotonic acid	206 242	13 500 250	ditto ditto
	Nitromethane	201 274	5 000 17	Methanol ditto
	Benzene	184 204 256	60 000 7 900 200	Cyclohexane ditto ditto

Table 4

Characteristic Frequencies of Functional Groups in I-R Region

Group	Wave number range, cm^{-1}	Intensity *
Valence oscillations of C—H		
Alkanes	2962-2853	s-m
Alkenes		
monosubstituted	3040-3010	m
	3095-3075	m
disubstituted		
cis-	3040-3010	m
trans-	3040-3010	m
gem-	3095-3075	m
trisubstituted	3040-3010	m
Alkynes	about 3300	m
Arenes	about 3060	var
Deformational oscillations of C—H		
Alkanes		
CH	about 1340	wk
CH_2	1485-1445	m
CH_3	1470-1430	m
	1380-1370	s
gem-dimethyl	1385-1380	s
	1370-1365	s
tert-butyl	1395-1385	m
	about 1365	s
Alkenes		
monosubstituted	995-985	s
	915-905	s
	1420-1410	s
disubstituted		
cis-	about 690	s
trans-	970-960	s
	1310-1295	m
gem-	895-885	s
	1420-1410	s
trisubstituted	840-790	s

Table 4, continued

Group	Wave number range, cm^{-1}	Intensity *
Alkynes	about 630	s
Arenes		
substitution type**		
five adjacent H atoms	about 750	var, s
	about 700	var, s
four adjacent H atoms	about 750	var, s
three adjacent H atoms	about 780	var, m
two adjacent H atoms	about 830	var, m
one H atom	about 880	var, wk
Valence oscillations of multiple bonds (C=C and C≡C)		
Alkenes		
unconjugated	1680-1620	var
monosubstituted	about 1645	m
disubstituted		
cis-	about 1645	m
trans-	about 1675	m
gem-	about 1655	m
trisubstituted	about 1670	m
tetrasubstituted	about 1670	wk
conjugated	1650	wk
	1600	wk
Alkynes		
monosubstituted	2140-2100	m
disubstituted	2260-2190	var, wk
Allenes	about 1950	m
	about 1060	m
Arenes	about 1600	var
	about 1580	var
	about 1500	m
	about 1450	m
Valence oscillations of C=O		
Ketones		
saturated aliphatic	1725-1705	s

Table 4, continued

Group	Wave number range, cm^{-1}	Intensity *
saturated cyclic		
6-membered (and over)	1725-1705	s
5-membered	1750-1740	s
4-membered	1775	
α,β-unsaturated aliphatic	1685-1665	s
α,β-unsaturated cyclic		
6-membered (and over)	1685-1665	s
5-membered	1724-1708	s
aryl	1700-1680	s
diaryl	1670-1660	s
α-diketones	1730-1710	s
β-diketones (enolic)	1640-1540	s
1,4-quinones	1690-1660	s
Aldehydes		
saturated aliphatic	1740-1720	s
α,β-unsaturated aliphatic	1705-1680	s
aromatic	1715-1695	s
Esters		
saturated aliphatic	1750-1735	s
saturated cyclic σ-lactones	1750-1735	s
unsaturated	1880-1770	s
vinyl esters type		
α,β-unsaturated and aryl	1720-1717	s
α-keto esters	1755-1740	s
β-keto esters (enolic)	about 1650	s
Carboxylic acids		
saturated aliphatic	1725-1700	s
α,β-unsaturated aliphatic	1715-1690	s
aromatic	1700-1680	s
Anhydrides		
saturated cyclic	1850-1800	s
	1790-1740	s
α,β-unsaturated and aromatic	1830-1780	s
aliphatic	1770-1720	s

Table 4, continued

Group	Wave number range, cm^{-1}	Intensity*
Acid halides		
acid fluorides	about 1850	s
acid chlorides	about 1795	s
acid bromides	about 1810	s
α,β-unsaturated and aromatic	1780-1750	s
	1750-1720	m
Amides		
primary		
solid or concentrated solutions	about 1650	s
dilute solutions		
secondary	about 1690	s
solid or concentrated solutions	1680-1630	s
dilute solutions	1700-1670	s
tertiary, solid or in solutions	1670-1630	s
Valence oscillations of C—H		
Aldehydes	2900-2820	wk
	2775-2700	wk
Valence oscillations of O—H		
Carboxylic acids	2700-2500	wk
Valence oscillations of N—H		
Amides		
primary unbonded group	about 3500	m
	about 3400	m
primary bonded group	about 3350	m
	about 3180	m
secondary unbonded group	about 3430	m
secondary bonded group	about 3320-3140	m
Deformational oscillations of N—H		
Amides		
primary (dilute solutions)	1620-1590	s
secondary (dilute solutions)	1550-1510	s

Table 4, continued

Group	Wave number range, cm^{-1}	Intensity*
Valence oscillations of C—O		
Esters		
acetates	1060-1000	wk
	1247-1236	s
formates	1200-1180	s
	1161-1152	m
propionates and higher homologues	1200-1163	s
α,β-unsaturated	1310-1250	s
	1200-1100	s
Valence oscillations of O—H		
Alcohols		
unbonded O—H groups	3650-3590	var, n
bonded by intermolecular bond with one bridge	3550-3450	var, n
polymer association	3400-3200	s, wd
bonded by inttramolecular	3570-3450	var, n
H-bond with one bridge	3200-2500	
chelates		wk, n
Deformational oscillations of O—H and valence oscillations of C—O		
Alcohols		
primary	about 1050	s
	about 1350-1260	s
secondary	about 1100	s
	1350-1260	s
tertiary	about 1150	s
	1410-1310	s
Phenols	about 1200	s
	1410-1310	s

Table 4, continued

Group	Wave number range, cm^{-1}	Intensity*
Valence oscillations of N—H		
primary unbonded	about 3500	m
	about 3400	m
secondary unbonded	3500-3310	m
Imines	3400-3300	m
Amine salts	3130-3030	m
Deformational oscillations of N—H		
Amines		
primary	1650-1590	s-m
secondary	1650-1550	wk
Amine salts	1600-1575	s
	1500	s
Valence oscillations of C—N		
Amines		
aromatic primary	1340-1250	s
secondary	1350-1280	s
tertiary	1360-1310	s
aliphatic	1220-1020	wk
	about 1410	wk
Valence oscillations of C≡N		
Alkyl nitriles		
saturated	2260-2240	m
α,β-unsaturated	2235-2215	m
Aryl nitriles	2240-2220	m
Isocyanates	2275-2240	m
Isocyanides	2220-2070	m
Valence oscillations of C=N		
Alkyl derivatives of imines and oximes	1690-1640	var
α,β-unsaturated compounds	1660-1630	var

Table 4, concluded

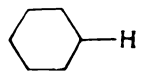
Group	Wave number range, cm^{-1}	Intensity*
Valence oscillations of N=N		
Azo compounds	1630-1575	var
Oscillations of $C-NO_2$		
Nitro compounds		
aromatic	1570-1500	s
	1370-1300	s
aliphatic	1570-1550	s
	1380-1370	s
Valence oscillations of S—H		
	2600-2550	wk
Valence oscillations of C—S		
	1200-1050	s
Valence oscillations of S=O		
Sulphoxides	1070-1030	s
Sulphones	1160-1140	s
	1350-1300	s
Sulphonamides	1180-1140	s
	1350-1300	s
Sulphonic acids	1210-1150	s
	1060-1030	s
	650	

* Abbreviations for intensity: s—strong, m—medium, wk—weak, var—variable, n—narrow, wd—wide.

** In addition, substituted benzenes produce peaks that are characteristic of each type of substitution and in the region of 2000-1650 cm^{-1}.

Table 5

Some Chemical Shifts

Proton	δ, ppm	Proton	δ, ppm
RCH_3	0.9-1	$R_2C{=}C(H)R$	~ 5.5
R_2CH_2	1.3-1.5		
R_3CH	2.0-2.5	$R_2C{=}C(CH_3)R$	~ 1.8
$R_2C{=}CH_2$	~ 5.0		
$R_2C{=}C(CH_2R)R$	~ 2.3	RCOOH	~ 11*
		$RCOOCH_3$	2.0
$R{-}C{\equiv}C{-}H$	2.5	$R{-}CH_2{-}NO_2$	4.4
$R{-}C{\equiv}C{-}CH_3$	2.0	$R{-}CH_2{-}N$	2.3-3.2
$R{-}CH_2Cl$	3.7		
$R{-}CH_2Br$	3.5		1.44
$R{-}CH_2I$	3.2		
$R{-}CHCl_2$	5.8		7.8
$R{-}OH$	~ 5*		
$R{-}O{-}CH_3$	3.3	$Ar{-}CH_3$	2.3
		$ArCH_2R$	2.7
$R{-}C(=O)H$	9.7	$Ar{-}CH_2{-}Cl$	4.5
		$Ar{-}CO{-}CH_3$	2.6
$R{-}CO{-}CH_3$	2.3	$Ar{-}OCH_3$	3.8

* Strongly depends on the temperature, concentration, and nature of the solvent.

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